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Source Assessment Ammonium Nitrate Production

Monsanto Research Corp, Dayton, Ohio

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SOURCE ASSESSMENT:
AMMONIUM NITRATE PRODUCTION

by

M. J. Search and R. B. Reznik

Monsanto Research Corporation
1515 Nicholas Road
Dayton, Ohio 45407

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EPA Task Officer: Ronald A. Venezia

Office of Energy, Minerals, and Industry
Industrial Environmental Research Laboratory
Research Triangle Park, North Carolina 27711

Prepared for

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Washington, DC 20460

PREFACE

The Industrial Environmental Research Laboratory (IERL) of EPA has the responsibility for insuring that pollution control technology is available for stationary sources to meet the requirements of the Clean Air Act, the Federal Water Pollution Control Act, and solid waste legislation. If control technology is unavailable, inadequate, or uneconomical, then financial support is provided for the development of the needed control techniques for industrial and extractive process industries. Approaches considered include: process modifications, feedstock modifications, add-on control devices, and complete process substitution. The scale of the control technology programs ranges from bench- to full-scale demonstration plants.

The Chemical Processes Branch of the Industrial Processes Division of IERL has the responsibility for investing tax dollars in programs to develop control technology for a large number (>500) of operations in the chemical industries. As in any technical program, the first question to answer is, "Where are the unsolved problems?" This is a determination which should not be made on superficial information; consequently, each of the industries is being evaluated in detail to determine if there is, in EPA's judgment, sufficient environmental risk associated with the process to invest in the development of control technology. This report contains the data necessary to make that decision for the air emissions from ammonium nitrate production.

Monsanto Research Corporation has contracted with EPA to investigate the environmental impact of various industries which represent sources of pollution in accordance with EPA's responsibility as outlined above. Dr. Robert C. Binning serves as Program Manager in this overall program, entitled "Source Assessment," which includes the investigation of sources in each of four categories: combustion, organic materials, inorganic materials, and open sources. Dr. Dale A. Denny of the Industrial Processes Division at Research Triangle Park serves as EPA Project Officer. In this study of ammonium nitrate production, Dr. Ronald A. Venezia served as EPA Task Leader.

ABSTRACT

This report describes a study of air pollutants emitted by the ammonium nitrate industry. The potential environmental effect of the source was evaluated using source severity (defined as the ratio of the maximum ground level concentration of an emission to the ambient air quality standard for criteria pollutants or to a modified 'TLV' for noncriteria pollutants).

Representative processes and an average plant were defined for the purpose of establishing a base on which to determine the emissions and severity of the source. The industry produces 39% of its original solution capacity as ammonium nitrate solutions and 61% as solids of which 92% are formed by prilling. The remaining 8% are formed by granulation or graining. Primary emissions from ammonium nitrate plants are particulates and ammonia. Processes releasing the greatest amount of emissions are the neutralizer (particulates and ammonia) and the prill tower (particulates). Emission factors were found to be highly dependent on individual plant operation.

This report was submitted in partial fulfillment of Contract No. 68-02-1874 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. The study described in this report covers the period April 1975 to July 1977.

CONTENTS

Preface		iii
Abstract		iv
Figures		vii
Tables		viii
Abbreviations and Symbols		x
I	Introduction	1
II	Summary	3
III	Source Description	6
	A. Process Description	6
	1. Introduction	6
	2. Ammonium Nitrate Production by Prilling	9
	3. Other Processes	17
	B. Materials Flow	19
	C. Average Plant Parameters	22
IV	Emissions	24
	A. Emissions from Each Process	24
	1. Neutraliser Operations	25
	2. Evaporator/Concentrator Operation	28
	3. Prilling Tower Operation	29
	4. Cooler and Dryer Operation	31
	5. Fugitive Emissions	31
	B. Low Density Prilling	33
	C. Potential Environmental Effect	34
V	Control Technology	41
	A. Particulates	41
	B. Ammonia or Nitric Acid	45
	C. Potential Impact of Controls	45
	D. Future Considerations	45

CONTENTS (continued)

VI Growth and Nature of the Industry 47

A. Present Technology 47
B. Emerging Technology 47
C. Industry Production Trends 48

References 50
Appendices

A. Raw Data Used to Calculate Emission Factors and Plant Characteristics 51
B. Derivation of Sorucs Severity Equations 57
C. Estimate of Steam from Neutralizer 61
D. Calculation of Affected Population 62

Glossary 64
Conversion Factors and Metric Prefixes 66

FIGURES

Number		Page
1	Flow diagram of ammonium nitrate production.	2
2	Generalized flow sheet of ammonium nitrate production processes.	7
3	Physical states of ammonium nitrate products.	8
4	Geographical distribution of ammonium nitrate plants.	9
5	Capacity distribution of ammonium nitrate plants.	10
6	Prilling process flow diagram.	11
7	Stengel reactor.	18
8	Materials flow diagram - prilled ammonium nitrate.	20
9	Source severity versus distance for the release of emissions from confinement for coating operation.	33
10	Source severity distribution for neutralisers used in making solutions and high density prills.	36
11	Source severity distribution for evaporator/ concentrators used in making solutions and high density prills.	36
12	Source severity distribution for high density prilling towers.	36
13	Source severity distribution for high density cooling drums.	37
14	Source severity distribution for the evaporator/ concentrator in low density prilling processes.	37
15	Prilling tower showing placement and operation of the CFCA collecting cone.	43
16	Full-scale Brink collection unit.	43
17	Brink high efficiency element collection efficiency.	44
18	Capacity and production trends.	48

TABLES

Number		Page
1	Capacity Distribution of Product Types	3
2	Particulate Emission Parameters for Average Production Operations	4
3	Size Analysis of Prilled Ammonium Nitrate	15
4	Polymorphic Changes of Ammonium Nitrate	16
5	Material Balance for Low Density Prilling Process	21
6	Material Balance for High Density Prilling Process	21
7	Emission Parameters for Ammonia from Neutralizer Exhaust Based on Approximation of pH	26
8	Emission Parameters for Ammonia from Neutralizer Exhaust Based on Source Testing	26
9	Emission Parameters for Particulates from Neutralizer Exhaust Based on Dissociation/ Recombination Theory	28
10	Emission Parameters for Particulates from Evaporator/Concentrator Based on Dissociation/ Recombination Theory	29
11	Operating Conditions Used to Obtain Data on Particulate Emissions from Prilling Tower Operations	30
12	Emission Parameters for Particulates from Prilling Tower	30
13	Particulate Emission Parameters for Low Density Prilling Operation	34
14	Particulate Emissions for Average Processes	35
15	Percent of Plants Exceeding Specified Values of Source Severity, S	38

TABLES (continued)

Number		Page
16	Particulate Emissions from Ammonium Nitrate Plants by State	39
17	Particle Size Distribution in the Neutralizer and High Density Prilling Tower Airstreams	41
18	Controlled Particulate Emissions	46
19	Production of Ammonium Nitrate by End Use, 1976	49
A-1	Ammonium Nitrate Plant Locations and Capacities	54
A-2	Ammonium Nitrate Plant Particulate Emission Factors	55
A-3	Prill Tower Emissions	56
A-4	Representative Stack Heights	56

ABBREVIATIONS AND SYMBOLS

A	-- the area around a plant site where the source severity, S, is ≥ 1.0, km^2
A'	-- one-half of the cross-sectional area of a building perpendicular to the flow of wind, m^2
AAQS	-- ambient air quality standard, $\mu g/m^3$
a, b, c	-- constants in the atmospheric dispersion equation for σ_z
D	-- distance downwind from a plant building to the plant boundary, km
D_p	-- population density, persons/km^2
E	-- emission factor, g/kg
e	-- 2.72
F	-- hazard factor, g/m^3
h	-- stack height, m
$\bar{h}$	-- average stack height, m
P	-- affected population
p	-- pressure, cm of Hg
Q	-- emission rate, g/s
Q_{total}	-- overall emission rate for an entire plant, g/s
S	-- source severity
S_{total}	-- overall source severity for an entire plant
T	-- absolute temperature, K
t	-- averaging time used in calculating $\bar{x}_{max}$, min
t_0	-- instantaneous averaging time of 3 min

ABBREVIATIONS AND SYMBOLS (continued)

TLV	-- threshold limit value, mg/m^3
$\bar{u}$	-- national average wind speed of 4.5 m/s
x, y, z	-- rectangular coordinates around a plant site; x is the wind direction, y is perpendicular to the wind direction, and z is the vertical direction, m
x_1, x_2	-- distances downwind where the source severity equals 1.0, m
a	-- the ratio $2/\pi e\bar{u}$
π	-- 3.14
σ_y	-- standard deviation of horizontal dispersion, m
σ_z	-- standard deviation of vertical dispersion, m
$\bar{x}$	-- average ground level concentration, $\mu g/m^3$
x_{max}	-- maximum ground level concentration, $\mu g/m^3$
$\bar{x}_{max}$	-- average maximum ground level concentration, $\mu g/m^3$
$(\bar{x}_{max})_{total}$	-- overall $\bar{x}_{max}$ for an entire plant
$x_{(x, o, o)}$	-- concentration downwind with no vertical or horizontal component

SECTION 1

INTRODUCTION

Ammonium nitrate (NH_4NO_3), made from ammonia (NH_3) and nitric acid (HNO_3) to give either liquid or solid product, is used in fertilizers as a source of nitrogen, in certain types of explosives, in the production of nitrous oxide, and in other miscellaneous applications.

This report evaluates the environmental impact of air emissions from ammonium nitrate production by identifying emission points, emission characteristics, and the process operating variables which affect the emissions. A set of criteria is developed to further evaluate the potential environmental effects of the emissions. The potential impact of available air pollution control equipment on emissions is also discussed.

SECTION II

SUMMARY

Total ammonium nitrate (100% NH_4NO_3) production in the U.S. for 1974 was 7.12×10^6 metric tons.[a] Major products were 2.78×10^6 metric tons of ammonium nitrate solution and 4.34×10^6 metric tons solid product. Ammonium nitrate was produced at 64 plant sites located in 30 states and 59 counties.

Figure 1 presents a flow diagram of the ammonium nitrate manufacturing process. Ammonia and 55% nitric acid react in a neutralizer to form a solution, and the heat of reaction concentrates the solution to 83% NH_4NO_3. The water given off in this process, as well as that given off by the following concentration step, is either exhausted to the atmosphere or condensed. The 83% solution is further concentrated to 95% or 99+% in an evaporator/concentrator. Solid ammonium nitrate particles can then be formed from the concentrated solution by graining, granulation, or prilling. Both high and low density prills are made, and together they account for >92% of the solid ammonium nitrate produced. High density prills (860 kg/m^3 bulk density) are made from a 99+% solution, while low density prills (770 kg/m^3 bulk density) are made from a 95% solution.

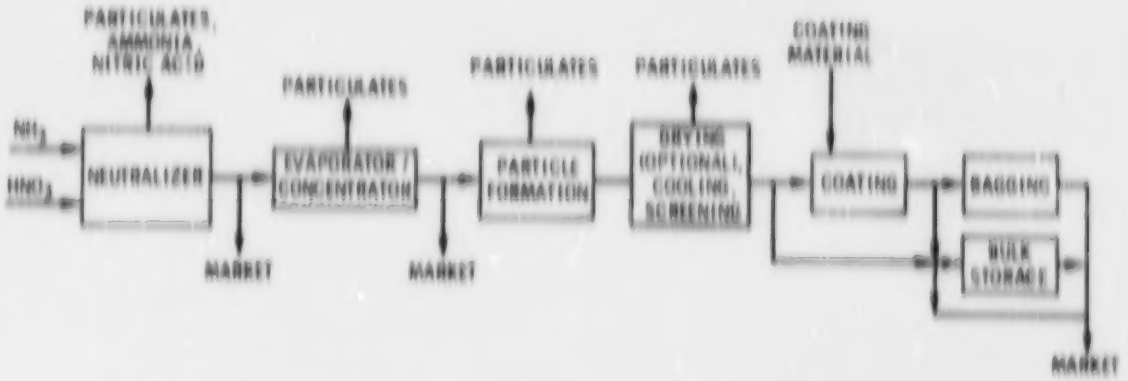

Figure 1. Flow diagram of ammonium nitrate production.

[a] 1 metric ton = 10^6 grams; conversion factors and metric system prefixes are presented at the end of this report.

After forming, the particles are dried (low density prills only), cooled, screened, and in some cases coated to enhance shelf life characteristics. In over 90% of high density prill production no coating takes place; rather, an additive is used to enhance shelf life. In a very few instances (<5%) coating is used with a prill containing an additive.

The finished product is stored in bulk or shipped in train hopper cars or bulk trucks. Less than 10% of the product is bagged in 23-kg to 45-kg quantities for shipment.

Ammonium nitrate plants produce several final product types. Available production facilities for each product type or combination thereof are distributed as presented in Table 1.

TABLE 1. CAPACITY DISTRIBUTION OF PRODUCT TYPES

Final product	Number of plants	Percent of total capacity
Solutions	18	26.7
Prills	13	40.8
Grains or crystals	5	5.1
Prills and solutions	24	23.7
Other combinations	4	3.6

An average ammonium nitrate plant has a solution capacity of 131,500 metric tons/yr and is located in a county with a population density of 209 persons/km^2. The average capacity of a high density prilling operation is 95,000 metric tons/yr, and the average for low density prilling is 62,700 metric tons/yr. The actual operating rate for a particular ammonium nitrate plant is a function of season and geographical area.

Emissions released during the manufacture of ammonium nitrate consist of particulates and either ammonia or nitric acid. Emission points are shown in Figure 1 and listed in Table 2 with the corresponding particulate emission factors (grams of particulate per kilogram of product) and emission rates. The level of uncertainty associated with the average emission factors for the neutralizer and prilling tower was obtained by applying the "student t" test to input data. The "t" test involves the estimation of the average value of a sample population and the establishment of confidence ranges within which the true average value is likely to exist.

Either ammonia or nitric acid is released from the neutralizer, depending on which reactant is present in excess. The average process uses ammonia in excess because it reduces particulate emissions and hence plume opacity. Ammonia emissions have been found to range from 0.026 to 1.14 g/kg, reflecting the wide variability in operations. Plants monitor the neutralization reaction

TABLE 2. PARTICULATE EMISSION PARAMETERS FOR AVERAGE PRODUCTION OPERATIONS

Emission point	Emission factor,[a] g/kg	Emission rate, g/s	χ_{max}, µg/m³	Source severity	Affected population, persons
Solutions and high density prills					
Neutraliser[b]	1.84 ± 0.849	6.88	519	4.07	95
Evaporator/concentrator[b]	0.47[c]	1.66	180	0.70	0
Prill tower[d]	1.17 ± 1.104	4.1	44	0.17	0
Cooler[d]	0.05[c]	0.15	16	0.06	0
Low density prills[e,f]					
Neutraliser	0.045	0.089	7.0	0.03	0
Evaporator/concentrator	0.088	0.17	17	0.06	0
Prill tower	0.496	0.987	10.6	0.04	0
Predryer	0.015	0.030	4.0	0.01	0
Dryer	0.009	0.018	1.7	0.01	0
Cooler	0.016	0.032	1.1	0.01	0
Coating	1.0[g]	6.0	ie[h]	0.14	0

[a] Emission factors are for uncontrolled operations except for predryer, dryer, and cooler.

[b] Parameters are based on an average neutraliser capacity of 131,500 metric tons/yr.

[c] Percent uncertainty not reported since value is determined by theoretical calculations.

[d] Parameters are based on average high density prilling capacity of 95,000 metric tons/yr.

[e] Parameters are based on average low density prilling capacity of 62,700 metric tons/yr.

[f] Percent uncertainty not reported since data are based on tests at one plant.

[g] Value based on material balance.

[h] Value of ground level concentration at plant boundary; coating is a source of fugitive emissions at ground level, and χ_{max} cannot be calculated.

by pH measurements, but may unintentionally release more ammonia than expected.

As a measure of potential environmental impact, the average maximum ground level concentration, χ_{max}, and the source severity, S, were determined for emissions from each process based on average capacities (Table 2). In the case of particulates, S is the ratio of χ_{max} to the ambient air quality standard (260 µg/m³). For ammonia the air quality standard is replaced by a reduced threshold limit value (TLV®); i.e., TLV × 8/24 × 1/100. The range of values of χ_{max} and S for ammonia are 89 µg/m³ to 1,003 µg/m³ and 0.1 to 17.2, respectively; particulate values are given in Table 2.

Those persons living in the area around a plant where the source severity exceeds 1.0 are termed the affected population. Values of the affected population for particulate emissions from the various processes are shown in Table 2. For ammonia emissions, this population may range from 0 to 1,058 persons.

The national and state emission burdens of the ammonium nitrate industry were determined for particulates. The national emission burden is the ratio of industry particulate emissions to total national particulate emissions from all stationary sources, expressed as a percent. The state particulate emission burden is the same ratio on a state-by-state basis. For the ammonium nitrate industry the national emission burden is 0.11%. The state emission burden for Nebraska is 1.2%. All others are below 1.0%; 80% are below 0.5%.

Control technologies with the capability of lowering particulate emissions have been developed for the ammonium nitrate industry. One system consists of a large collection cone in the prill tower and a Brink® mist eliminator with a 98.6% removal efficiency to treat a combined stream consisting of the prill tower, neutraliser, and evaporator/concentrator exhausts. With this equipment, the combined stream has a source severity of 0.10.

A second control method for the prill tower exhaust employs scrubbers on the top of the tower. Pilot plant tests have shown efficiencies >90%. Coupled with this system is a redesigned neutralizer that emits particulates in quantities 10 to 20 times lower than conventional neutralisers. The high efficiency wet scrubbers that are usually used on dryer and cooler exhausts have a removal efficiency of at least 99%.

Ammonium nitrate production is expected to increase at a rate of 2.0%/yr through 1978. With no additional controls, particulate emissions will be 11% greater in 1978 than in 1972. However, since plants are adding controls, and because of a possible shift in emphasis from solid to liquid ammonium nitrate, 1978 emissions may be lower than those of 1972.

SECTION III

SOURCE DESCRIPTION

A. PROCESS DESCRIPTION

1. Introduction

Four major processes for producing ammonium nitrate are currently used in the United States. Three of these (prilling, graining, and granulation by spheroidisation) have a common starting point in that they first produce an 83% ammonium nitrate solution which is then concentrated to either a range of 95% to 96% or >99.5%. They then differ in the manner by which the solid product is formed. The fourth, the Stengel process, differs from these three in the method by which the feed reactants are mixed and concentrated as well as in the solid formation method.

A generalised flow sheet of these four ammonium nitrate processes is shown in Figure 3. Other known processes that are either obsolete or not in use in the U.S. are: crystallisation, the Fauser process, the Bamag-Meguin A.G. process, and pan granulation. These will not be treated in this investigation.

This assessment of ammonium nitrate production centers on the prilling process, since at least 92% of all solid ammonium nitrate in the U.S. is produced by this method. Other ammonium nitrate manufacturing processes utilise essentially the same initial process steps as prilling; i.e., neutralisation and concentration. The remaining processes (graining, granulation by spheroidisation, and Stengel granulation) are discussed in Section III.A.3.

In the prilling process, ammonium nitrate is produced by the following exothermic reaction of ammonia and nitric acid:

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 \qquad (1)$$

When a 55% nitric acid feed stream is used, the product of the above reaction is an aqueous solution of ammonium nitrate (61%). In practice the heat of reaction (108.8 kJ) is used to drive off a portion of the water and concentrate the solution to 83% ammonium nitrate.

Two solid products can be made by the prilling process: low density prills and high density prills. The basic difference in

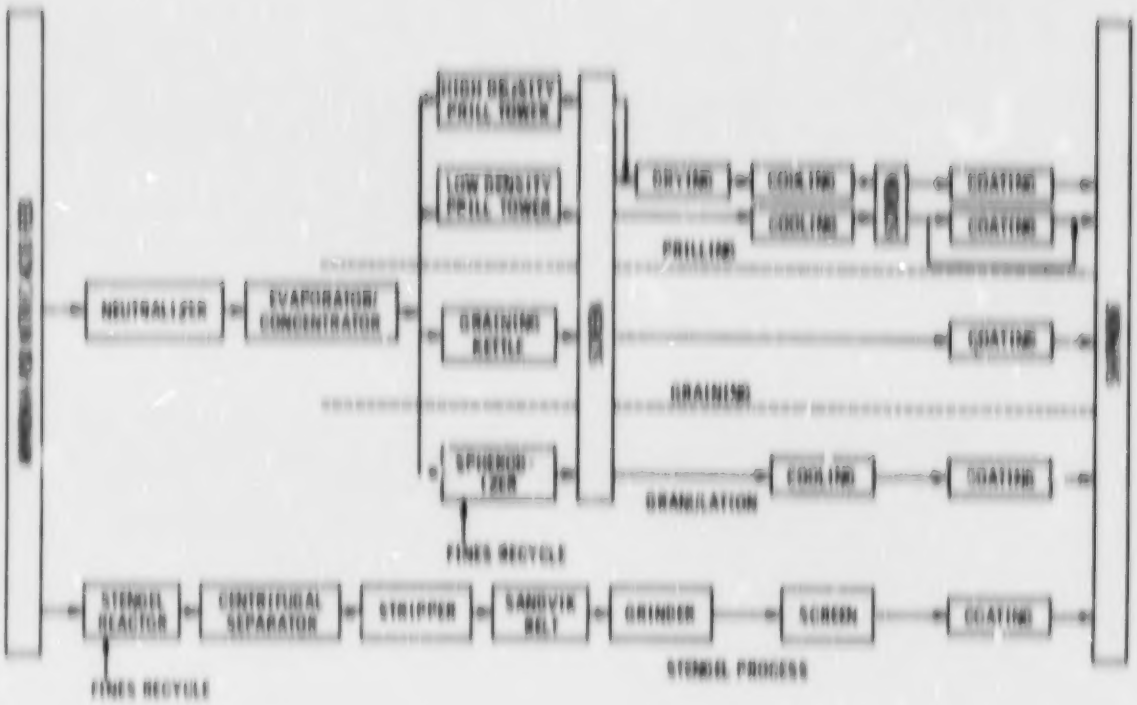

Figure 3. Generalized flow sheet of ammonium nitrate production processes.

production is the solution concentration entering the prill tower. For low density material, a 95% to 96% ammonium nitrate solution is sprayed into the prill tower. As the droplets descend and cool, the ammonium nitrate solidifies, trapping water in the solid prills. The water evaporates when the prills are dried, leaving void space which results in prill bulk density of 770 kg/m^3. Approximately 40% of all prilled ammonium nitrate is low density material. The same process is used for high density prills except that more concentrated ammonium nitrate solution is used (99.5+%). This results in less void space and produces prills with bulk density of 860 kg/m^3. Approximately 60% of all prilled ammonium nitrate is high density material.

After solidifying, prills are screened to remove oversize and undersize material. Low density prills then go to a two-stage drying process to drive off excess water, followed by cooling and additional screening. High density prills do not require the drying step and go directly to cooling followed by screening.

Low density prills which are not used as an on-site intermediate (e.g., in explosive manufacturing or fertilizer mixing) are coated

with diatomaceous earth or other material as a water barrier. High density prills are generally not coated (<3% are coated); instead, they are formulated with an additive to enhance shelf life.

The final product may be stored in warehouses (for a short period of time), shipped in bulk railroad cars or bulk trucks, or bagged in 23-kg or 45-kg quantities.

In 1974, 84 plants produced 7.13×10^6 metric tons of solution in terms of 100% NH_4NO_3. (1) Figure 3 illustrates the final physical states of the solution based on actual production and indicates that 92% of all solid product is formed by prilling, 7% by granulation, and 1% by graining.

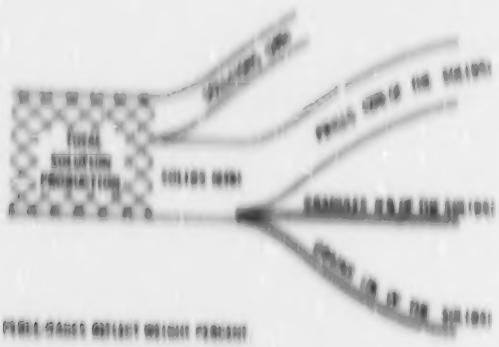

Figure 3. Physical states of ammonium nitrate products.

Field observations[a] and discussions with experts in the industry indicate that particulate emissions (per unit product) from prilling are greater than those from graining, Stengel granulation or granulation by spherodization. Presumably this is because prilling places greater stresses on the liquid than do the other processes, resulting in smaller particles. This fact, in conjunction with the high air flow rates used in prilling compared with other processes, makes prilling a worst case situation in terms of emissions. Therefore, only prilling emissions have been studied in detail in this assessment because they provide an upper limit of emissions.

---

[a]Four presurveys were conducted at various plant locations to inspect different ammonium nitrate manufacturing methods and to observe the quantities of emissions from the different processes. These field observations are referenced in this report.

* * * * * * * * * *

(1) Personal communication with E. A. Harre, National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, Alabama, June 1976.

Table A-1 (Appendix A) lists the 64 U.S. ammonium nitrate plants by company name and location (city, state, and county or parish), and includes county or parish population densities and annual total solution capacities. The geographical distribution of ammonium nitrate plants is shown in Figure 4 (1).

Figure 4. Geographical distribution of ammonium nitrate plants.

A frequency distribution of plant sizes is presented in Figure 5, indicating the mean, median, and mode plant capacities. At least 60% of the plants have capacities less than or equal to the mean, 131.5 x 10^3 metric tons/yr. The diversity in the final product types made at each site has previously been shown in Table 1; this information is based on a confidential Monsanto Company survey.

2. Ammonium Nitrate Production by Prilling

The basic prilling process (2) consists of spraying hot, concentrated ammonium nitrate solution from the top of a tower. During their descent countercurrent to a lower temperature airstream, the droplets are formed into spherical particles between 84 μm and 2.38 mm in diameter. (One industry contact mentioned that occasionally particles >3.36 mm were manufactured.) This basic procedure is actually only one step of what is termed the prilling process today, which includes the following:

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(2) Williams, L., L. F. Wright, and H. Hendriks. Process for the Production of Ammonium Nitrate. U.S. Patent 2,402,192 (to Consolidated Mining and Smelting Co. of Canada, Ltd.), June 18, 1946.

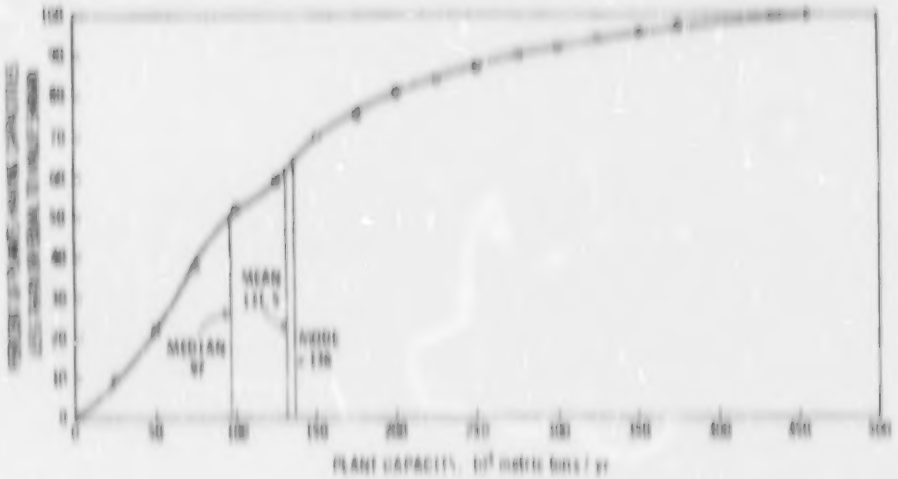

Figure 5. Capacity distribution of ammonium nitrate plants.

- Feed preparation and recycle
- Neutraliser and liquid storage
- Evaporation/concentration
- Particle formation
- Product preparation
- Dust control

The above areas are distinguished as six sections on the generalised flow sheet in Figure 6 by dashed lines (3). Existing dust control systems are discussed later in Section V.

a. Feed Preparation and Recycle Loops--
Section 1 in Figure 6 contains the feed pretreatment and the recycle loops entering the main process stream before the neutraliser. The liquid ammonia feed is heated to vaporisation by one of several methods. In some processes, part of the liquid ammonia is passed through a coil placed in the neutraliser steam exhaust, and the remainder is used as refrigerant for the air supplying the cooler. The temperature of the ammonia feed stream is 66°C to 77°C.

Nonprilling processes utilise countercurrent, U-tube, horizontal heat exchangers, either one or two in series. The series arrangement is used primarily for those processes requiring superheated feeds; e.g., the Stengel process.

(3) Sheseron, W. H., Jr., and W. B. Dunwoody, Ammonium Nitrate, Industrial and Engineering Chemistry, 45(3):496-504, 1953.

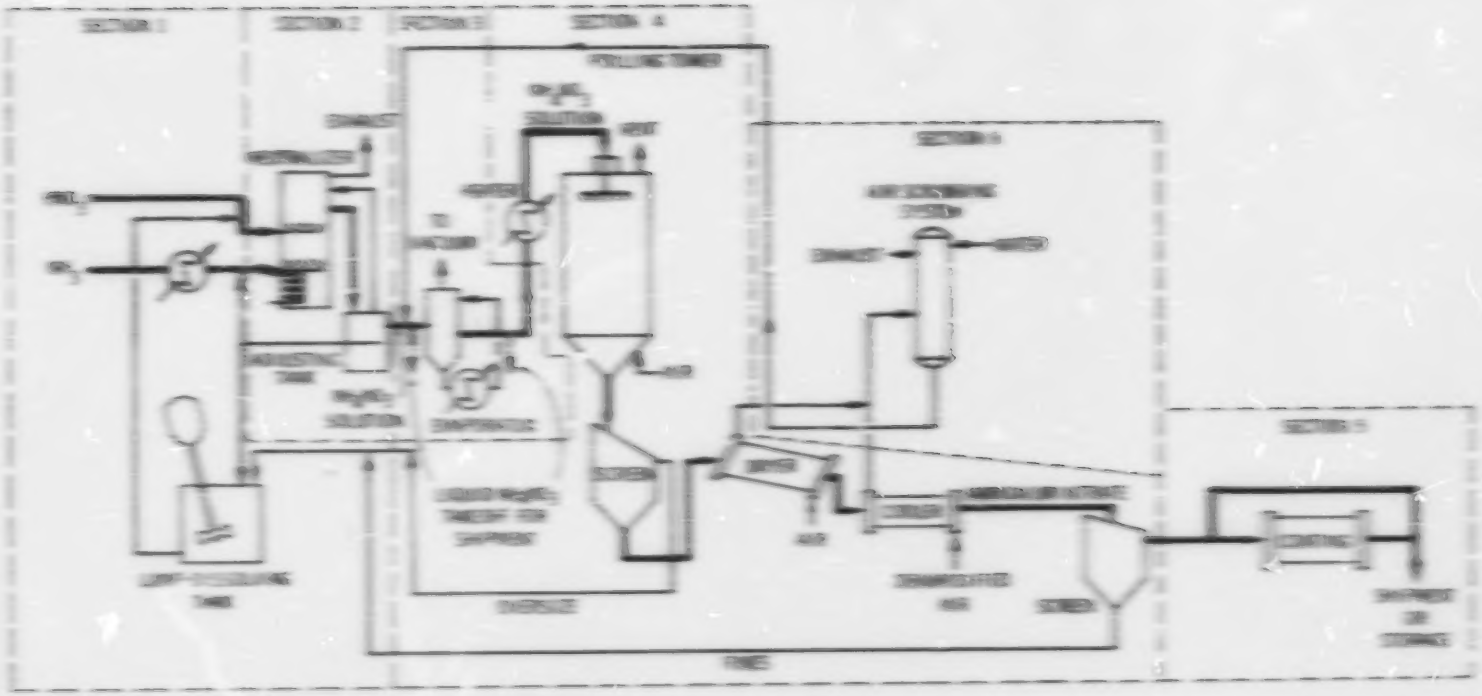

Figure 6. Prilling process flow diagram.

Nitric acid feed (55%) may be heated or unheated. In most cases (>85%) it is heated, using a preheater, to ~82°C (it is usually below 88°C to prevent extreme acid corrosion).

A lump-dissolving tank recycles the oversize and undersize material resulting from screening the prill tower product. The oversize and fine materials enter the tank, dissolve, and are sent to the neutraliser or evaporator/concentrator as a weak (~60%) recycle liquor. In some plants, this tank is a sealed unit with an agitator. In other plants it is simply an open collection pool at the bottom of the tower.

Some ammonium nitrate facilities are portions of entire nitrogen fertiliser complexes consisting of ammonia, nitric acid, ammonium nitrate, and urea plants. In such cases the feed to the ammonium nitrate unit may come from the urea process. This occurs in <20% of the facilities, however, and will not be considered standard operating procedure.

b. Neutraliser and Adjusting Tank--
Section 2 of Figure 6 contains the neutraliser and an adjusting tank. The neutraliser is a vertical, stainless steel vessel 1.8 m to 3.7 m in diameter and 4.6 m high. Its size is dependent upon other design considerations in the individual plant. The ammonia gas is introduced into the neutraliser below the nitric acid nozzle. The reaction, in effect, is carried out under a hydrostatic head of ammonium nitrate solution by placement of the solution overflow pipe at the appropriate height (see neutraliser in Figure 6). Agitation is achieved by the feed sprays and water vapor created by the heat of reaction. Since the reaction is exothermic ($NH_3 + HNO_3 \rightarrow NH_4NO_3 +$ 108.8 kJ), the heat is sufficient to concentrate the ammonium nitrate leaving the neutraliser to 83% and produce steam that leaves the reactor and, in some plants, heats the ammonia feed as previously described.

The neutraliser can be operated with a slight excess of ammonia or of nitric acid. When operating with nitric acid in excess, the solution pH is automatically controlled at 1.5 by a recorder-controller which actuates a valve in the nitric acid line. When operating with an ammonia excess, the pH of a condensed sample from the offgases is manually maintained between 9.5 and 11.0. Industrial sources are quick to point out that pH control is not easy. At the neutral point, the pH titration curve is nearly vertical. In addition, the pH probes have an approximate 94°C temperature limit, and the liquor must be condensed and cooled carefully so that salting does not occur.

Under normal operating conditions, the neutraliser temperature is maintained at 121°C either by adding the weak (~60%) ammonium nitrate recycle liquor or by varying the nitric acid feed strength. To minimise ammonium nitrate decomposition, the maximum temperature permitted during abnormal operating periods is 149°C. When impurities arising from low grade nitric acid feed are present (such as copper, zinc, oil, wood, cotton, and chloride impurities)

the neutraliser temperature is held to a maximum of 141°C in periods of abnormal operation. (In normal practice, low grade nitric acid is not used as a feed stream.)

The coil in the bottom of the neutraliser is used only when the unit is shut down or when necessary to keep the ammonium nitrate in solution. Heat can be introduced to the neutraliser by passing steam through this coil during startup to facilitate ammonia vaporization. Water may also be introduced directly into the neutraliser for emergency shutdown.

The adjusting tank is used to store the 83% ammonium nitrate solution from the neutraliser, to receive the overflow from the head tank on the prilling tower, and supply the evaporator/concentrator on a demand basis. The actual concentration in such tanks may therefore range from 81% to 83%.

c. Evaporator/Concentrator--
Section 3 in Figure 6 consists of the evaporator/concentrator. In this portion of the process the 81% to 83% ammonium nitrate solution from section 2 is concentrated to a 95% to 96% solution for low density prill production or to a 99.5+% solution for high density prill production. Liquid ammonium nitrate for use as a nitrogen source in liquid fertilizer can be taken from the process before or after the evaporator/concentrator, as shown in Figure 6, giving solution concentrations of 83% or 95% to 96%, respectively.

The unit shown in Figure 6 is a vacuum, film-type evaporator used by >75% of the ammonium nitrate production facilities. It operates at 57 kPa using a single steam-jet ejector and produces a 95% ammonium nitrate product. However, this is not the only method used for solution concentration. Other options include: (1) a concentrator with in-tank agitation, (2) two-stage evaporation that gives a product with 7% moisture after the first stage and 4% to 5% moisture after the final stage, and (3) barometric condensers as an adjunct to vacuum evaporators to condense the water removed from the exhaust stream. Concentration to 99.5% for high density prills is achieved in a similar manner using different operating parameters.

d. Particle Formation--
As shown in section 4 of Figure 6, particle formation includes the prilling tower, various sizing screens, and the dryer and cooler. Each of these areas is discussed below.

(1) Prilling tower--In the early days of the prilling industry, tower design was accomplished primarily by trial and error. Consequently the towers in use today show a great variation in size, shape, and operating parameters. However, the basic operating principle of all such towers is the same. Ammonium nitrate solution pumped to a head tank at the top of the tower maintains a constant pressure on a spray device that sprays the solution into

the tower. Droplets are formed and fall countercurrent to a rising airstream. The airstream acts as a heat transfer mechanism that cools the ammonium nitrate below its melting point and permits solidification of the droplet into a spherical particle.

The first prilling tower constructed was a 6.1-m-square, 21-m-high wooden unit. The tallest tower in use today is 61 m high and the shortest recent design is 21 m high (4). Towers of circular, square, or rectangular cross section are presently in operation.

Originally the solution was forced into the prilling tower by spraying it upward through nozzles at an angle of 0.785 rad to the horizontal. This arrangement is not essential, however. Good results have since been obtained with the spray angled upward or downward, or directed straight downward. Most (>90%) prilling towers spray at a downward angle or straight downward to eliminate much of the impingement problem (3). The actual form of the spray device ranges from a single nozzle to multiple nozzles or a spray bucket.

Ducts at the tower bottom supply an airflow countercurrent to the drops, primarily as a temperature control. The air may be washed and filtered prior to tower introduction; however, this is not common practice since the additional moisture may inhibit drying of the prills. The air moving upward cools the prills from an inlet solution temperature of up to 186°C to an outlet prill temperature of 75°C. The temperatures used in each plant vary according to such factors as humidity, ambient temperature, and type of product being made. As the drop falls, the air suddenly chills its surface, causing a crust to form. One modification to this design permits the drops to fall through a section of tower containing a quiescent zone of heated air. Fifty percent of the towers have such quiescent zones, ranging from 3 m to 8 m in length. Airflow rates in prill towers are highly variable. An average range of flow rates, however, is 5,960 to 11,600 std. m^3/metric ton. Air velocities in prill towers also cover a range of values, from 1.37 to 2.45 m/s or higher depending on the tower geometry and airflow rate.

The design of prilling towers is complex and many variables which affect the tower performance must be considered, including:

- Prill tower geometry
- Liquid inlet temperature
- Desired prill exit temperature
- Airflow rate
- Air inlet temperature

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(4) Sharp, J. C. Nitrogen. In: Chemistry and Technology of Fertilizers, V. Sauchelli, ed. Reinhold Publishing Corporation, New York, New York, 1960. pp. 26-32.

- Air inlet humidity
- Quantity of material to be produced
- Desired prill size distribution

(3) Sizing screens--In the majority of the prilling plants (>90%), two sets of screens (as shown in Figure 6) are used to regulate the prill size. A 9.51-mm screen at the bottom of the prill tower discharges to the drying system after it removes the oversize material for recycle to the lump-dissolving tank. The 1.68-mm screen after the cooler rejects material smaller than 0.55 mm. These fines are also recycled to the lump-dissolving tank. Table 1 presents size distributions of the prills before and after screening; i.e., the final product.

TABLE 1. SIZE ANALYSIS OF PRILLED AMMONIUM NITRATE

Screen size (standard sieve mesh designation)		Percentage of sample retained on screen						
		Unscreened material			Screened material			
		High density[a]		Low density[b]	High density[c]			Low density[b]
		Sample A[b]	Sample B[b]		Sample A[b]	Sample B[b]	Sample C[d]	
2.38 mm	(8)	9.12	8.29	7.17	11.03	5.73	2.24	10.29
1.68 mm	(10)	27.61	33.38	27.25	40.56	34.79	13.15	40.66
1.41 mm	(12)	53.29	41.43	34.05	47.66	44.58	33.73	36.76
250 µm	(60)	9.92	16.87	31.04	0.69	14.90	51.53	12.21
88 µm	(170)	0.028	0.015	0.024	0.002	0.010	0.143	0.059
74 µm	(200)	0.009	0.015	<0.001	0.001	0.009	0.070	<0.001
44 µm	(325)	<0.001	0.007	<0.001	<0.001	<0.001	0.070	<0.001
44 µm	(pan)	<0.001	<0.001	<0.001	<0.01	<0.001	0.076	<0.001
TOTAL		100.00	100.01	99.98	99.96	100.01	99.95	100.00

[a] Sample characteristic of the material leaving the prill tower.

[b] Samples obtained from a plant operating line.

[c] Sample characteristic of product leaving the plant.

[d] Sample obtained from local fertilizer dealer in a 22.7-kg bag. Note increase in fine size and shift in screened quantities to finer size, possibly as a result of prill breakage caused by additional handling.

(3) Drying--Dryers are used only in the production of low density prills since the purpose of this operation is to drive off the water trapped in the prill during solidification. The temperature must be increased progressively as the moisture content declines to avoid deterioration of the crust through moisture transfer and subsequent caking. In most cases (>95%) this is achieved by a two-stage dryer arrangement. Thus, the temperature in the pre-dryer and dryer can be closely controlled to minimize prill destruction.

A second reason for close temperature control is the change in ammonium nitrate crystal structure with temperature. Prill destruction can result from specific volume changes associated

with the crystal transition points shown in Table 4 (5). The temperature sensitivity of the crystal structure can be modified by placing an additive in the solution before it enters the prill tower. The most common additives in use today are magnesium oxide and calcium oxide (3). Certain companies, however, have their own additives based on proprietary formulations. The additive also eliminates the diurnal cycle of size change when prilled ammonium nitrate is stored in warm weather.

TABLE 4. POLYMORPHIC CHANGES OF AMMONIUM NITRATE (5)

Phase reaction	Type of modification	Temp., °C
Melt ↔ I	Liquid↔cubic	169.6
I ↔ II	Cubic↔tetragonal	125.4
II ↔ III	Tetragonal↔α-orthorhombic	84.4
III ↔ IV	α-Orthorhombic↔β-orthorhombic	32.4
IV ↔ V	β-Orthorhombic↔pseudohexagonal	-17.9
II ↔ IV	Tetragonal↔β-orthorhombic	50.6

Rotary hot-air drum dryers are used in at least 80% of the ammonium nitrate facilities requiring predryer and dryer installations. These dryers are equipped with lifting flights to tumble the prill bed while warm air flows countercurrent to the material flow. Two basic configurations are used for predryers, dryers, and coolers. The first is a stacked arrangement in which the material exiting from the predryer falls into the dryer and that from the dryer falls into the cooler. An alternate configuration carries the exit material from one dryer to the other by a network of conveyor belts. This arrangement offers greater flexibility for processing both low density and high density prills (which require only a cooler) on the same process line.

(4) Cooling--Two types of coolers are used in the ammonium nitrate industry. Rotary drum coolers are used in most installations, but a recently available fluidized bed cooler has been installed in over 30 processes worldwide in the last 5 years. In either unit, the air quality is carefully monitored to prevent excess humidity from entering the cooler.

e. Product Preparation--
Section 5 of Figure 8 consists of a coating drum and any preshipment packaging facilities required. Coating materials consist primarily

(5) Miller, P., and W. C. Saeman. Properties of Monocrystalline Ammonium Nitrate Fertilizer. Industrial and Engineering Chemistry, 40(1):154-160, 1948.

of diatomaceous earth (3), fatty amine-clay mixtures (6), or limestone dust (7). They serve as water barriers for the hygroscopic prills. In the case of uncoated prills an additive is placed in the spray solution, as previously described. The industry is currently using in varying degrees several proprietary additives other than magnesium oxide and calcium oxide. Permalene-34, a mixture of boric acid, diammonium phosphate, and aluminum sulfate, is marketed by Mississippi Chemical Corporation. The "NUCLO-ADD" process, marketed by C & I Girdler, Inc., causes heterogeneous nucleation by adding inert organics to the melt. Magnesium nitrate and various other proprietary additives are also used. In addition to their effect on temperature sensitivity, additives also reduce the hygroscopicity of the material, but only to a limited extent. Therefore, some products containing an additive may also be coated.

Over 90% of the high density material produced is shipped or stored in bulk form. Bagging is performed periodically, but only when the plant is in the center of its market area where small users buy bagged product. Bulk product is loaded by conveyor through a tube into train hopper cars or bulk trucks.

3. Other Processes

As shown earlier in Figure 1, approximatley 8% of the total solid ammonium nitrate produced is grained or granulated. The two products differ basically in crystal form. The grained particles have longer fiber characteristics while the granules are more spherical.

a. Graining--
The graining process employs feed streams and a neutralizer similar to those used in the prilling process. Following neutralization, the ammonium nitrate solution is sent to an open-pan or falling film evaporator. The open-pan evaporator is simply an open pan equipped with steam coils. The falling film evaporator is a vertical tube and shell heat exchanger with the 83% NH_4NO_3 solution entering on the tube side. Steam is used for heat on the shell side and air passes countercurrently on the tube side, facilitating evaporation.

The evaporators produce a 98% NH_4NO_3 solution in batch operation. The solution is discharged to kettles approximately 2.1 m in diameter, equipped with large plows to keep the material stirred

(6) Black, A. V. Fertiliser Developments and Trends - 1968. Noyes Development Corporation, Park Ridge, New Jersey, 1968. 405 pp.

(7) Ammonium Nitrate. In: Riegel's Handbook of Industrial Chemistry, J. A. Kent, ed. Van Nostrand Reinhold Company, New York, New York, 1974. pp. 100-101.

as it cools and solidifies. Small amounts of stearic acid or other material may be added in the graining kettles to minimize the formation of undesired large grains. The vessel jacket is equipped with steam and cooling coils to control the cooling rate.

Temperatures used in graining can reach 152°C to 155°C. The final product is a small grain between 0.55 mm and 1.60 mm, which is screened, mixed with clay, and bagged.

b. Granulation--

(1) Stengel process--The Stengel process is used by very few plants in the industry on only about 2% of the total ammonium nitrate production.

In this process the ammonia vapor and nitric acid (58%) are preheated in separate heat exchangers and fed simultaneously and continuously to the Stengel reactor shown in Figure 7 (8, 9). The heat of reaction vaporizes the water in the nitric acid feed. A solution of 98% ammonium nitrate and trace ammonia flows from the reactor to a centrifugal separator which removes the ammonium nitrate and runs it through an air stripper that reduces the moisture content to approximately 0.2% (10).

Figure 7. Stengel reactor (9).

(8) Hester, A. S., J. J. Dorsey, Jr., and J. T. Kaufman. Stengel Process Ammonium Nitrate. Industrial and Engineering Chemistry, 46(4):622-633, 1954.

(9) Stengel, L. A. Process for Producing Ammonium Nitrate. U.S. Patent 2,568,901 (to Commercial Solvents Corp.), September 25, 1951.

(10) Dorsey, J. J. Ammonium Nitrate by the Stengel Process. Industrial and Engineering Chemistry, 47(1):11-17, 1955.

The molten ammonium nitrate flows into a weir box for distribution onto an endless, stainless steel, water-cooled (Sandvik) belt. Solid ammonium nitrate is removed from the belt by a doctor blade. This material is fed to the grinders, then screened, coated, and bagged. The oversize material is recycled to the grinder and the fines are returned to the process. Particle formation may also be accomplished using a prill tower, as described previously.

(2) Spheroidization--In this process, a 99.5% ammonium nitrate solution from a neutralizer and evaporator/concentrator, as previously described, is sprayed into a rotating drum containing ammonium nitrate granules. The drum is equipped with lifting flights that lift the granules and permit them to fall through the open space in the drum. The melt is applied to the granules in midair and in the bed. Ambient temperature is chilled to 7°C and passed countercurrently to cool the melt and solidify the granules. The particles exit the drum at <0.5% moisture which minimizes the amount of drying. Then the product is screened, cooled, coated, and bagged.

Solid particle formation by graining, granulation, and spheroidization will not be considered further in this assessment for the following reasons: 1) since emissions from these processes are lower than those from prilling, a consideration of high density prilling will give a maximum value of emissions; 2) these three processes account for less than 8% of total ammonium nitrate production; and 3) each of these processes is operated inside a building, and their only emissions are fugitive.

B. MATERIALS FLOW

A materials flow diagram of the prilling process is shown in Figure 8 based on the process flow diagram shown in Figure 6. As noted previously the dryer section (including the predryer and dryer) is not present in the high density prilling process. In this case streams 11 and 12 would be absent and stream 13 would be equivalent to stream 10. Table 5 lists approximate flow rates and compositions of each stream in Figure 8 for the production of low density ammonium nitrate using stoichiometric quantities of both reactants. Table 6 lists approximate flow rates and compositions for each applicable stream in Figure 8 for the production of high density ammonium nitrate using stoichiometric quantities of both reactants.

In both Tables 5 and 6 a coating application is assumed. If no coating is actually done, the final product weight is found in stream 17. The basic assumptions used to calculate these values are as follows:

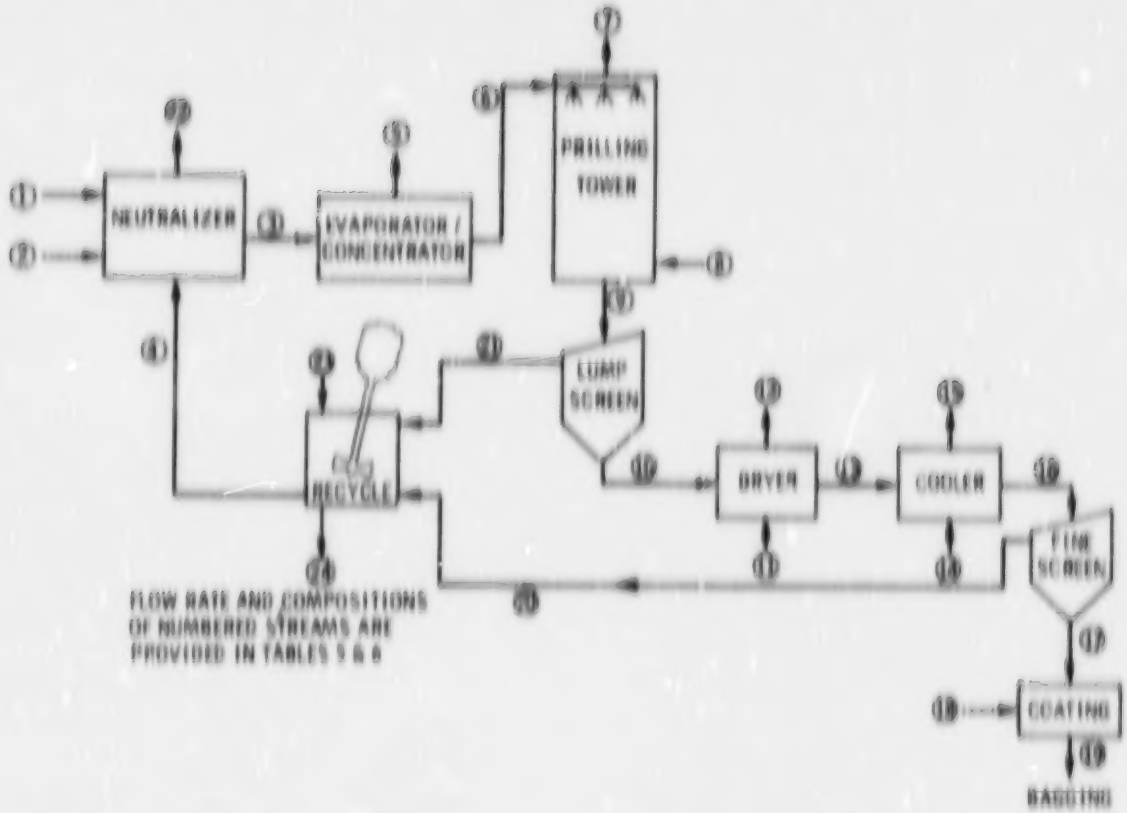

Figure 8. Materials flow diagram - prilled ammonium nitrate.

- Nitric acid feed is 55% nitric acid (3).
- All steam produced as a result of the heat of reaction exits from the neutraliser stack and does not condense and return to the neutraliser.
- Any excess reactants are negligible.
- Recycle stream 4 contains only ammonium nitrate and water.
- Any impurities present are negligible.
- Airflows to the dryer and cooler are given the values of X and Y since no change in weight through the equipment is expected.
- There is little or no moisture removal in the prill tower (3).
- Approximately 0.5% of the material produced by the prill tower is lost through the stack.

TABLE 5. MATERIAL BALANCE FOR LOW DENSITY PRILLING PROCESS (kg/hr)

Stream	Name	Ammonia	Nitric acid	Water	Ammonium nitrate	Air[a]	Other
1	Ammonia feed	1,134	0	0	0	0	0
2	Nitric acid feed	0	4,309	2,687	0	0	0
3	Concentrator feed	0	0	2,160	9,000	0	0
4	Recycle	0	0	230	959	0	0
5	Concentrator exhaust	0	0	1,000	0	0	0
6	Prill tower feed	0	0	230	9,959	0	0
7	Prill tower exhaust	0	0	0	50	[illegible]	0
8	Air for prill tower	0	0	0	0	[illegible]	0
9	Wet product	0	0	230	9,909	0	0
10	Dryer feed	0	0	200	9,670	0	0
11	Air to dryer	0	0	0	0	[illegible]	0
12	Dryer exhaust	0	0	130	50	[illegible]	0
13	Cooler feed	0	0	70	9,650	0	0
14	Air to cooler	0	0	0	0	[illegible]	0
15	Cooler exhaust	0	0	50	50	[illegible]	0
16	Dry product	0	0	20	9,600	0	0
17	Coating feed	0	0	0	9,671	0	0
18	Coating material	0	0	0	0	0	[illegible]
19	Final product	0	0	0	9,671	0	[illegible]
20	Fines recycle	0	0	0	50	0	0
21	Lump recycle	0	0	0	50	0	0
22	Neutralizer exhaust	0	0	1,210	50	0	0
23	Makeup solution[c]	0	0	250	101	0	0
24	Purge stream[d]	-	-	-	-	-	-

[a]Airflows to the dryer and cooler are given the value of 0 and V since no change in weight through the equipment is expected.

[b]Quantities of air feed to dryer and cooler not available.

[c]Makeup solution may be water or weak (<60%) ammonium nitrate solution or a combination of the two.

[d]Composition of stream determined by process requirements and contamination present in recycle vessel.

TABLE 6. MATERIAL BALANCE FOR HIGH DENSITY PRILLING PROCESS (kg/hr)

Stream	Name	Ammonia	Nitric acid	Water	Ammonium nitrate	Air[a]	Other
1	Ammonia feed	1,134	0	0	0	0	0
2	Nitric acid feed	0	4,309	2,687	0	0	0
3	Concentrator feed	0	0	2,160	9,000	0	0
4	Recycle	0	0	230	959	0	0
5	Concentrator exhaust	0	0	1,000	0	0	0
6	Prill tower feed	0	0	230	9,959	0	0
7	Prill tower exhaust	0	0	0	50	[illegible]	0
8	Air for prill tower	0	0	0	0	[illegible]	0
9	Wet product	0	0	230	9,909	0	0
10	Cooler feed	0	0	0	9,671	0	0
11	Air to cooler	0	0	0	0	[illegible]	0
12	Cooler exhaust	0	0	0	50	[illegible]	0
13	Dry product	0	0	0	9,621	0	0
14	Coating feed	0	0	0	9,671	0	0
15	Coating material	0	0	0	0	0	[illegible]
16	Final product	0	0	0	9,671	0	[illegible]
17	Fines recycle	0	0	0	50	0	0
18	Lump recycle	0	0	0	50	0	0
19	Neutralizer exhaust	0	0	1,210	50	0	0
20	Makeup solution[c]	0	0	250	101	0	0
21	Purge stream[d]	-	-	-	-	-	-

[a]Airflow to the cooler is given the value of V since no change in weight through the equipment is expected.

[b]Quantity of air feed to the cooler not available.

[c]Makeup solution may be water or weak (<60%) ammonium nitrate solution or a combination of the two.

[d]Composition of stream determined by process requirements and contamination present in recycle vessel.

- Approximately 0.5% of the material produced by the prill tower is recycled due to oversize (3).
- The ammonium nitrate losses from the dryer and cooler are 1% each based on the exit material from each unit.
- All water is evaporated by the time the product leaves the dryer.
- Approximately 0.5% of the material produced by the cooler is recycled because of its fine size (3).
- There is no loss from the coating drum.
- Coating application is approximately 3% of the final product weight.

Operating conditions are highly related to temperature. Most (>90%) of the neutralization is done at atmospheric pressure or with only a slight hydrostatic head. All of the other operations are performed at atmospheric pressure; therefore, temperature is the prime control.

In the neutraliser the temperature is maintained at 131°C by release of steam generated from the heat of reaction (108.8kJ) and the addition of recycle liquor. Temperature rises slightly in the evaporator to ~140°C; this can vary depending on the ammonium nitrate concentration of the exiting solution. In the prilling tower, the temperature of the prill drops from 140°C to 75°C thus placing the solution well below the solidification temperature of 123°C to 125°C (for a 95% ammonium nitrate solution).

Temperatures in the drying section (where applicable) and cooler are carefully monitored. Prill destruction could result from changes in specific volume associated with a phase change between tetragonal and α-orthorhombic forms if the temperature rises above 84.4°C, and between α-orthorhombic and β-orthorhombic forms if the temperature falls below 32.4°C. Therefore the temperature from the predryer through the cooler is kept between these two limits.

C. AVERAGE PLANT PARAMETERS

Although the ammonium nitrate industry manufactures a wide range of products, certain average plant parameters can be defined. An average plant has a neutraliser solution capacity of 131,500 metric tons/yr and is located in a county having a population density of 209 persons/km^2. (See Appendix A for a complete list of plant capacities and locations.) As shown in Table 1, there is no representative product. However, the average high density prilling operation has a capacity of 95,000 metric tons/yr, and the average low density prilling operation has a capacity of 62,700 metric tons/yr. Low density product is coated, but ~3% of the high density material is similarly treated.

Feedstock to the process in the average plant consists of a superheated ammonia stream at 70°C and a preheated nitric acid stream at 82°C. These reactants combine in a neutralizer to produce an 83% NH_4NO_3 stream which passes through a falling film evaporator for concentration to 99.5+% NH_4NO_3 to make high density product, or to 95% for low density product, and then passes into a prilling tower. The prills encounter a quiet zone 3 m long, then fall countercurrent to a cooling airstream for 34 m and exit through a cooler for bulk storage or direct loading into railroad hopper cars or bulk trucks. Scrubbers on the exhaust streams from the cooler, and from the drying section in the case of low density product, are the only controls used. Such scrubbers (to be described in Section V) have an efficiency of 97% to 98% (weight) and produce no visible emissions. A flow diagram has been presented in Figure 6.

Average stack heights (derived from the raw data presented in Table A-4) are as follows:

Neutralizer	15.2 m ± 30%	
Evaporator/concentrator	13.7 m ± 10%	
Prill tower	41.2 m ± 18%	
Dryer	13.7 m ± 15%	(if present)
Cooler	13.2 m ± 15%	
Loading car[a]	3.3 m ± 5%	

Other factors that interact and affect the operation of ammonium nitrate plants and the resulting emission rates include but are not restricted to:

- Prill tower geometry
- Temperature and moisture content of the various process streams
- Amount of coating required
- Airflow rates through the different processes
- Amount and species of reactant in excess
- Amount of hydrostatic head in neutralizer and tower
- Ambient temperature and relative humidity at plant site
- Type of spraying device
- Location of individual plant's market
- Requirements of individual plant's market
- Desired prill size distribution

All of the above variables can change the operating and physical characteristics of a plant without changing the basic flow diagram.

[a]Loading car stack height is determined by approximating height of a standard railroad car used in transporting this material.

SECTION IV

EMISSIONS

The manufacture of ammonium nitrate can emit particulates (NH_4NO_3), ammonia, and nitric acid mist. Particulates are released from the neutraliser, evaporator/concentrator, prilling tower, drying system, and cooler. Ammonia or nitric acid mist may be released from the neutraliser and the evaporator/concentrator, depending upon which reactant is present in excess. The chemical species (NH_3 or nitric acid mist) and quantity emitted are primarily dependent upon the individual unit operation and conditions. The majority (~75%) of ammonium nitrate plants operate under basic pH conditions (NH_3 excess). The quantity of ammonia emitted varies from plant to plant since it is directly related to the amount of ammonia in excess.

A. EMISSIONS FROM EACH PROCESS

In Figure 8, streams 5, 7, 13, 15, and 22 are shown as emission points from the ammonium nitrate process. These streams are the exhausts from the evaporator/concentrator, prilling tower, dryer, cooler, and neutraliser, respectively. In addition, fugitive emissions are released from screening, coating, bagging, and bulk loading operations. Each of these operations occurs within a building, and any emissions would exhaust from doors and windows rather than through a stack.

The following sections characterise the species emitted from each process and determine average emission factors. Average maximum ground level concentrations ($\bar{x}_{max}$) are calculated for emissions from each point, based on average emission factors and process parameters; i.e., production rates and stack heights. In addition, the source severity, S, defined as the ratio of $\bar{x}_{max}$ to the ambient air quality standard, AAQS, is determined for emissions from each operation. Where no air quality standard exists (NH_3, HNO_3), a reduced TLV is used in place of the AAQS; i.e., TLV x 8/24 x 1/100. The methodology for computing $\bar{x}_{max}$ and S is presented in Appendix B.

Percent uncertainty was established by applying a "Student t" test to the input data. The "t" test involves the estimation of the true average value of a sample population and the establishment of confidence ranges within which the true average value likely

exists (11). The "t" test is applied to the report data because the sample size is less than 30 and may not be normally distributed.

1. Neutralizer Operations

The exhaust gas from the neutralizer is a jet of superheated steam containing ammonia and particulates; i.e., droplets of recombined NH_3 and HNO_3 molecules liberated by dissociation. The steam acts as a carrier gas for the ammonia and particulates. Ammonia is released rather than HNO_3 because NH_3 is used as the excess reactant in most (>75%) of the plants.

a. Ammonia--
Data on ammonia emissions from the neutralizer have been obtained from three distinct sources. One source indicated that plants (neutralizers) operating on the basic or high pH side have lost as much as 4 kg of ammonia per metric ton of nitric acid consumed (2). For an average plant, 1.04×10^5 metric tons of acid are consumed per year, resulting in an anticipated ammonia loss of 4.14×10^3 metric metric tons/yr. For continuous operation this results in an emission rate of 13.1 g/s and an emission factor of 3.14 g of NH_3 per kg of NH_4NO_3 produced. The concomitant χ_{max} and source severity, derived using Equation 5 in Appendix B, are 1.3 mg/m^3 and 17.2 respectively.

A second method of estimating the ammonia released by the neutralizer is to approximate the quantity of ammonia contained in the neutralizer offgas by pH. The neutralizer offgas is normally held between a pH of 9.5 and 11 as discussed previously. This is the pH of a condensed sample of the offgas at 81°C. An ammonia solution with a pH of 10.6 is ~0.01N and contains 0.17 g NH_3/l, or 170 g NH_3/m^3. The total amount of steam leaving the neutralizer as a result of heat of reaction is calculated from a material balance to be 1.45 m^3/s for an average plant. Another author has reported a lower steam rate of 1.62 m^3/s (12), presumably because part of the steam condensed before leaving the neutralizer stack. (See Appendix C for calculations.) If the total amount of steam leaving the neutralizer were condensed, it would equal 0.85 kg to 1.82 kg of water per second. Combining this value with the ammonia concentration of 170 g/m^3, the emission rates (Q) of 0.15 and 0.32 g/s are determined. The emission factor (E), maximum ground level concentration (χ_{max}), and source severity (S) are listed in Table 7 for the two steam rate conditions discussed.

(11) Volk, W. Applied Statistics for Engineers, Second Edition. McGraw-Hill Book Co.; New York, New York, 1969. 154 pp.

(12) Metzger, T. R. Controlling Airborne Emissions from Ammonium Nitrate Production. Presented to Ammonium Nitrate Study Group, Sarnia, Ontario, August 1974. 7 pp.

TABLE 7. EMISSION PARAMETERS FOR AMMONIA FROM NEUTRALISER EXHAUST BASED ON APPROXIMATION OF pH

Parameter	Steam rate 1.67 m³/s	Steam rate 3.45 m³/s
Emission rate, g/s	0.15	0.32
Emission factor, g/kg	0.04	0.08
$\bar{x}_{max}$, ug/m³	12.1	25.8
Source severity	0.2	0.4

The third method of determining ammonia emissions is by source testing. The tests conducted found concentrations between 100 ppm and 3,000 ppm NH_3 in the neutraliser exhaust, which are equivalent to 0.072 g/m³ and 2.16 g/m³, respectively. These yield the emission parameters shown in Table 8.

TABLE 8. EMISSION PARAMETERS FOR AMMONIA FROM NEUTRALISER EXHAUST BASED ON SOURCE TESTING

Parameter	Steam rate 1.67 m³/s	Steam rate 3.45 m³/s
NH_3 concentration in neutraliser exhaust, ppm	100 to 3,000	100 to 3,000
Emission factor, g/kg	0.026 to 0.86	0.055 to 1.8
Emission rate, g/s	0.1 to 1.5	0.2 to 7.5
$\bar{x}_{max}$, ug/m³	0.9 to 280	19 to 580
Source severity	0.1 to 4.6	0.2 to 9.8

Two factors need to be considered in interpreting these data. Ammonia was initially used as the excess reactant because it was inexpensive and it also produced a significantly less visible plume. (Excess ammonia vaporizes and inhibits the dissociation reaction, $NH_4NO_3 \rightarrow NH_3 + HNO_3$; the recombination of NH_3 and HNO_3 vapor is the main source of particulates.) While the economic aspect is no longer true, plants without controls still tend to run on the basic side because of the lower plume opacity obtained.

Secondly, those plants operating on the basic side tend to run with an appreciable excess of ammonia. This premise has been

confirmed in cases where testing was done and measurements showed 1,000 ppm of NH_3 in the exhaust gas. In each case, the company involved did not realize that it was losing so much ammonia and took corrective measures to lower the ammonia emissions.

It should be noted that the operation of the neutraliser is a relatively subjective art rather than a science. Therefore, the emissions variation resulting from and directly dependent upon the plant operations can be significant from plant to plant and from operator to operator. For example, one source test indicated a range on the same neutraliser of 150 ppm to 1,000 ppm of NH_3 in the offgas depending upon when the sample was taken (results varied both from shift to shift and within individual shifts).

b. Particulates--
Particulate emissions from the neutraliser consist of ammonium nitrate particles. Trace metal emissions resulting from the corrosion of the neutraliser were discounted since, even at parts per billion concentrations, the quantity leaving the neutraliser would be sufficient to cause equipment failure. The ammonium nitrate particulate emission was determined by two methods: source testing and dissociation theory. Some source testing has been completed and the results are listed in Appendix A. From these data, an emission factor of 1.64 g/kg ± 84% can be calculated. For the average plant, this results in Q = 6.85 g/s, χ_{max} = 539 $\mu g/m^3$, and S = 2.07.

The second method for estimating particulate emissions utilizes dissociation theory and assumes that all of the material dissociated will end up as recombined droplets leaving the stack. While this method cannot be used to supersede test data, it is a valuable verification tool.

The vapor pressure (p, in cm of Hg) of ammonium nitrate can be estimated using the following equation (11):

$$\log_{10} p = - \frac{4,103}{T} + 8.502 \qquad (2)$$

where T = absolute temperature, K

Assuming ideality and that steam and vapors are in equilibrium, emission rates of 3.14 g/s and 1.48 g/s are calculated for steam rates of 1.62 m^3/s and 3.45 m^3/s, respectively. This results in the following values in Table 9 for emission factor, maximum ground level concentration and source severity.

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(11) Feick, G., and R. M. Hainer. On the Thermal Decomposition of Ammonium Nitrate. Steady-State Reaction Temperatures and Reaction Rate. Journal of the American Chemical Society, 76(23):5860-5863, 1954.

If the two calculated theoretical extremes are averaged with the source test data, an emission factor of 1.41 g/kg ± 76% can be obtained, which results in a source severity of 1.76. While this average cannot be taken as a true value, it demonstrates the excellent agreement of theory to actual data available.

TABLE 9. EMISSION PARAMETERS FOR PARTICULATES FROM NEUTRALIZER EXHAUST BASED ON DISSOCIATION/ RECOMBINATION THEORY

Parameter	Value
Emission factor, g/kg	0.36 to 0.77
χ_{max}, µg/m³	120 to 260
Source severity	0.45 to 0.96

c. Nitric Acid--
Nitric acid is not normally added in excess to the neutralizer because it results in higher particulate emissions which in turn make the plume more visible. (Nitric acid is not vaporized as readily as ammonia and therefore does not suppress the dissociation of ammonium nitrate.) Consequently, there are no source test data available on the magnitude of HNO_3 emissions. The maximum level can be determined from a material balance, based on the fact that plants operating with excess acid use only 0.02% to 0.05% in excess. The emission factor for an average plant is ≤0.26 g/kg and the source severity (using TLV = 5 mg/m³ and h = 14 m) is ≤0.8. This calculation must be viewed as the maximum for the whole operation rather than just for the neutralizer since some of the excess HNO_3 may be released beyond the neutralizer.

2. Evaporator/Concentrator Operation

a. Particulates--
Few data are available on particulate emissions from evaporator/ concentrators primarily due to the wide variation in the types of evaporators employed. One can theoretically calculate the amount of particulates liberated as a result of dissociation and recombination since the operation is basically one of vaporization. The theory as proposed for neutralizers is valid in this case also. However, for these calculations, the amount of steam released can only be approximated by a material balance. For an average plant, ~1.5 m³/s of steam is released. With a vapor pressure of 56.2 Pa (5.5×10^{-4} atm), as determined by Equation 2, and a temperature of 143°C, an emission rate of 1.96 g/s is derived. Table 10 lists the resultant values for emission factor, maximum ground level concentration, and source severity.

TABLE 10. EMISSION PARAMETERS FOR PARTICULATES FROM EVAPORATOR/CONCENTRATOR BASED ON DISSOCIATION/ RECOMBINATION THEORY

Parameter	Value
Emission factor, g/kg	0.47
χ_{max}, ug/m^3	190
Source severity	0.7

The variations in operation of the evaporator/concentrator are similar to those present in the neutraliser. Another variation in the evaporator/concentrator that is not so predominant in the neutraliser is equipment design. As previously mentioned, ~75% of the industry utilises vacuum, film-type evaporators. The variation possible in the design of these evaporators is large. Other variation possibilities include the use of in-tank agitation, two-stage evaporation, or barometric condensers as an adjunct to vacuum evaporators. In the last case, emissions do not reach the atmosphere directly, but pass into the cooling tower. Therefore, sampling of the evaporator/concentrator to obtain data characteristic of the industry is difficult, if not impossible.

The source test results for evaporator/concentrators shown in Appendix A are a factor of ten lower than this theory predicts. However, a review of industry comments showed that the value predicted by theory is closer to average plant operations. Therefore, this value is used in further calculations as a maximum level of particulate emissions from the evaporator/concentrator.

b. Ammonia--
Ammonia should not be emitted from the evaporator/concentrator in any appreciable quantities, because the feed to the evaporator has a pH of ~5.2 to 5.4. This low pH is the result of ammonia vaporisation in the neutraliser. In addition, no ammonia odor was detected during field investigations.

3. Prilling Tower Operation

a. Particulates--
More emission tests have been run on the prilling tower than on any of the other potential emission points. Data obtained from these source tests are presented in Table A-2. In addition, data were received on the emissions from a high density prill tower during experimental studies where the operating conditions were varied in an attempt to identify relationships between certain process variables and emissions. These data are presented in

Table A-1. While no significant correlations were identified, many data were obtained on the particulate emissions for various melt pH's, spray temperatures, airflow rates, and additives in the ranges given in Table 11.

TABLE 11. OPERATING CONDITIONS USED TO OBTAIN DATA ON PARTICULATE EMISSIONS FROM PRILLING TOWER OPERATIONS

Process condition	Range of values
Spray pH	5.4 to 7.0
Spray temperature	171 to 186°C
Tower airflow	2,209 to 3,880 standard m^3/min
Additive addition	0.10 to 0.14 wt. % additive in melt

The conditions listed above were varied in a range characteristic of those found throughout the industry. Consequently, the data obtained are similar to those which would be expected from different high density prill towers within the industry. By including these data with those presented in Table A-2, the emission parameters shown in Table 12 were calculated for an average high density prilling operation; i.e., one having an annual capacity of 95,000 metric tons/yr.

TABLE 12. EMISSION PARAMETERS FOR PARTICULATES FROM PRILLING TOWER

Parameter	Value
Emission factor, g/kg	1.37 ± 10.0%
Emission rate, g/s	4.1
X_{max}, $\mu g/m^3$	44
Source severity	0.17

b. Ammonia--
Ammonia emissions from the dissociation in the melt at the top of the prill tower are insignificant. During field investigations, ammonia odors were not detectable at the top of the prill tower. The odor threshold of ammonia is reported to be 20 ppm to 53 ppm (14, 15) which corresponds to a source severity range of 0.09

(14) Ammonia. In: The Merck Index, P. G. Stecher, ed. Merck and Company, Inc., Rahway, New Jersey, 1968. p. 64.

(15) Matheson Gas Data Book. The Matheson Company, Inc., East Rutherford, New Jersey, 1966. pp. 13-22.

to 0.4 based on an average prill tower height of 41.2 m and an airflow rate of 2,209 to 3,880 m^3/min. If residual ammonia is estimated to be ~1% of the particulate emissions (i.e., assuming that 99% of the NH_4NO_3 that dissociates in the prill tower recombines), the source severity is <0.01. Under certain conditions, small quantities of ammonia are added to the melt to facilitate prilling. This procedure may raise the ammonia emissions slightly, but not above the odor threshold as indicated.

4. Cooler and Dryer Operation

Few test data are available on particulate emissions from coolers and dryers because these operations are routinely controlled with high efficiency scrubbers that give no visible plume. The only test measurement reported gives an uncontrolled emission factor of 5.13 g/kg for a cooler (16). This value agrees with others reported for uncontrolled dryers in the fertilizer industry (as well as in other mineral industries), which generally range between 1 g/kg and 10 g/kg (16).

Standard rotary dryers and coolers are usually controlled by high efficiency wet scrubbers with anticipated efficiencies of >99% for the removal of particles above 10 μm. There are several plants (<10%) that utilize lower efficiency (85%) scrubbers; however, the high efficiency scrubbers dominate. Assuming a conservative efficiency estimate of 99% for the previously reported uncontrolled emission factor (5.13 g/kg) results in a controlled emission factor of 0.05 g/kg and a source severity of 0.06 for the average cooling process.

The above emission factor can also be applied to the dryers used in the production of low density prills. In this case, the source severity is 0.04.

5. Fugitive Emissions

In addition to the stack emission points discussed above, there are two potential sources of nonstack or fugitive-type emissions: the coating operations and the bulk loading operations. No particulate emissions could be seen during plant visits; however, no actual test data are available. A worst case emission factor is therefore derived from material balance considerations.

(16) Point Source Listings. National Emissions Data System. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1974.

a. Coating Operations--
All low density prills and ~3% of all high density prills are coated with one of several coating materials. At an average low density prilling operation, therefore, 1.99 kg/s of prilled material would be coated. With an average coating rate of 3%, 0.06 kg/s of coating would be applied to the prills.

If all the coating material is lost to the atmosphere through doors and windows (a worst case assumption), an emission rate of 60 g/s results. By employing the relevant equations for emissions from buildings (developed in Appendix B), the following relationships are derived:

$$\bar{x}_{max} = 63.0\ p^{-1.814} \qquad (3)$$

and

$$S = 2.42 \times 10^{5}\ p^{-1.814} \qquad (4)$$

A graph of the source severity equation is shown in Figure 9. For the source severity to be <1.0, the distance from the building to the plant boundary must be more than 929 m. The effect of the building cross-sectional area on this distance is minimal. For comparison the average plant is situated a distance of 800 m from the nearest plant boundary. (Plants have been built in remote areas because of explosive hazards.)

In this case, a worst case assumption is unrealistic because the coating material must adhere to the prills to be effective. Industrial contacts involved in coating operations indicate that a loss of 10% of the coating material is a liberal estimate, and most of this falls to the floor of the coating building. For this reason, an emission rate of <6 g/s is an upper limit for actual coating operations. The impact of this change is demonstrated by the second line drawn on Figure 9 using a 6 g/s emission rate. The distance from the source where the source severity is <1.0 is then 461 m.

b. Bulk Loading Operations--
Table 7 indicated the size distribution of the final product exiting the ammonium nitrate process. As can be seen, <0.001% of the material on the belt leaving the plant is <44 μm. From Stokes law it can be calculated that the distance required for 44 μm particulates to settle is 7.1 m, based on a wind speed of 4.5 m/s and a loading height of 6.2 m. This is well inside the typical plant boundary, so that emissions that remain airborne must have an emission factor of <0.01 g/kg.

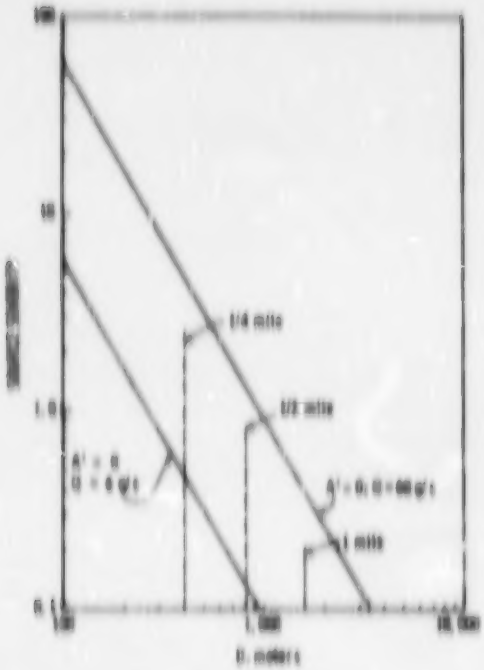

Figure 9. Source severity versus distance for the release of emissions from confinement for coating operation.

B. LOW DENSITY PRILLING

Data in previous sections described plants making ammonium nitrate solutions and high density prills. This sections presents a brief consideration of strictly low density prilling. Section 4 of Figure 3 is a flow diagram for a low density prilling operation. A careful inspection of this schematic reveals the same emission points as those of a high density operation, but with the inclusion of a dryer or a drying system consisting of a predryer and dryer in series.

Source test data obtained at a low density ammonium nitrate facility are given in Table 13. Each emission factor is an average based on two to four tests per unit. Note that only particulate emissions were measured. (Ammonia emissions will be proportional to the amount of excess ammonia added to the neutralizer.) Average ground level concentrations and source severities are also given in Table 13, and it can be seen that these are lower than those for high density prill production.

TABLE 13. PARTICULATE EMISSION PARAMETERS FOR LOW DENSITY PRILLING OPERATION[a]

Unit	Emission factor, g/kg	Emission rate, g/s	$\bar{x}_{max}$, $\mu g/m^3$	S
Neutralizer[b]	0.045	0.089	7.0	0.01
Evaporator/concentrator[b]	0.088	0.17	17.0	0.06
Prilling tower[b]	0.456	0.987	10.6	0.04
Predryer[c]	0.015	0.030	2.9	0.01
Dryer[c]	0.009	0.018	1.7	0.01
Cooler[c]	0.016	0.032	3.3	0.01

[a] Emission rate, $\bar{x}_{max}$, and source severity values were calculated using the capacity and stack heights for an average low density prilling operation; i.e., 62,700 metric tons/yr.

[b] Uncontrolled.

[c] Controlled.

It is believed that the lower emission factors for low density prill production result from lower operation temperatures in the manufacturing process. In the manufacture of high density prills, higher temperatures are required to keep the concentrated ammonium nitrate solutions in the liquid state. Particulates are generated by the dissociation and subsequent recombination of NH_4NO_3 molecules at elevated temperatures. Lower operating temperatures therefore reduce particulate emission. If a low density production line was maintained at the same temperature used for high density production, its particulate emissions would increase to the levels observed for high density prilling.

C. POTENTIAL ENVIRONMENTAL EFFECT

There are several ways in which the potential environmental effect of emissions from the production of ammonium nitrate can be evaluated: 1) by the magnitudes of $\bar{x}_{max}$ and source severity, S; 2) by the number of persons in the vicinity of a plant who may be affected by an emission; and 3) by the amount of state and national industry emissions.

Source severity has been defined previously as the ratio of $\bar{x}_{max}$ to the appropriate ambient air quality standard (260 $\mu g/m^3$ in the case of particulates) or to a reduced TLV (18 mg/m^3 x 8/24 x 1/100 in the case of ammonia). It indicates the relative environmental severity of different air emissions.

Table 14 summarizes the particulate emission factors, emission rate, $\bar{x}_{max}$ values, and source severities for the average processes used in making solutions and high density prills.

TABLE 14. PARTICULATE EMISSION PARAMETERS FOR SOLUTION AND HIGH DENSITY PRILLING OPERATIONS

Emission characteristic	Emission point			
	Neutraliser	Evaporator/ concentrator	Prilling tower	Cooler
Emission factor, g/kg	1.64[a]	0.47[a]	1.37[a]	0.05[b]
Emission rate, g/s	6.85	1.96	4.13	0.15
$\bar{\chi}_{max}$, µg/m³	539	190	44	16
Source severity	2.07	0.70	0.17	0.06
Affected population, persons	95	0	0	0

[a]Uncontrolled. [b]Controlled.

Values are for uncontrolled emissions except in the case of the cooler that is controlled with a scrubber as discussed previously. The corresponding values for ammonia emissions from the neutraliser are as follows:

- Emission factor: 0.026 to 3.14 g/kg
- Emission rate: 0.1 to 13.1 g/s
- $\bar{\chi}_{max}$: 8.9 to 1,030 µg/m³
- Source severity: 0.1 to 17.2

The higher severity for ammonia (17.2) corresponds to 1.5% excess ammonia in the feed stream. Plants do not operate this way intentionally because of the economic loss, and a well-monitored operation will exhibit a much lower source severity, i.e., below 1.0.

The data show that in ammonium nitrate manufacture the highest severities result from ammonia and particulate emissions from the neutraliser.

The impact of coating operations can be determined by evaluating the source severity at the plant boundary. Since an average plant has a boundary at least 800 m from the source, the source severity for coating is 0.14.

In addition to severities for average process operations, it is possible to calculate the distribution of severities for the whole industry. Figures 10 through 13 show source severity distributions for operations used in the manufacture of solutions and high density prills. The severity distribution curve for low density evaporator/concentrators is illustrated in Figure 14. Other low density operations are not shown because severities are <0.1 (although one prill tower has a severity of 0.11). Distributions were calculated from average emission factors and stack heights for each type of operation and the distribution of production

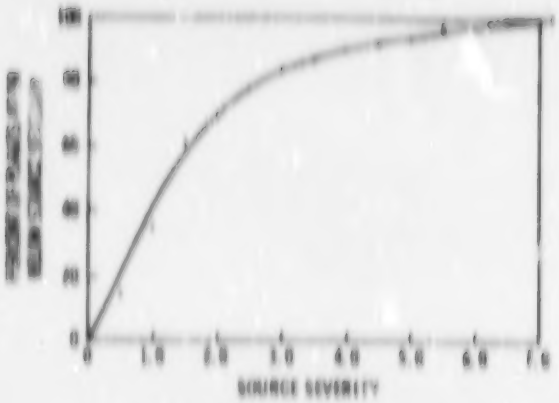

Figure 10. Source severity distribution for neutralisers used in making solutions and high density prills.

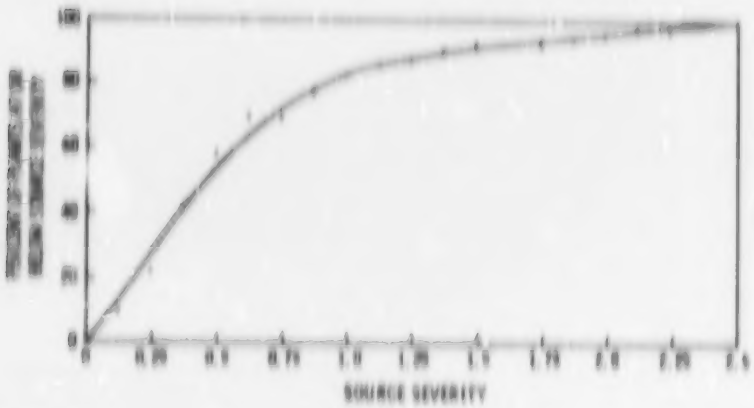

Figure 11. Source severity distribution for evaporator/concentrators used in making solutions for high density prills.

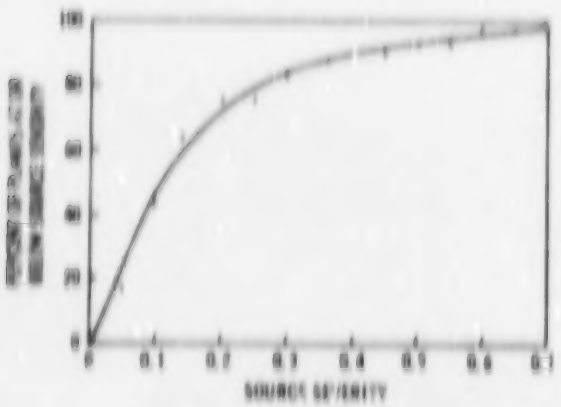

Figure 12. Source severity distribution for high density prilling towers.

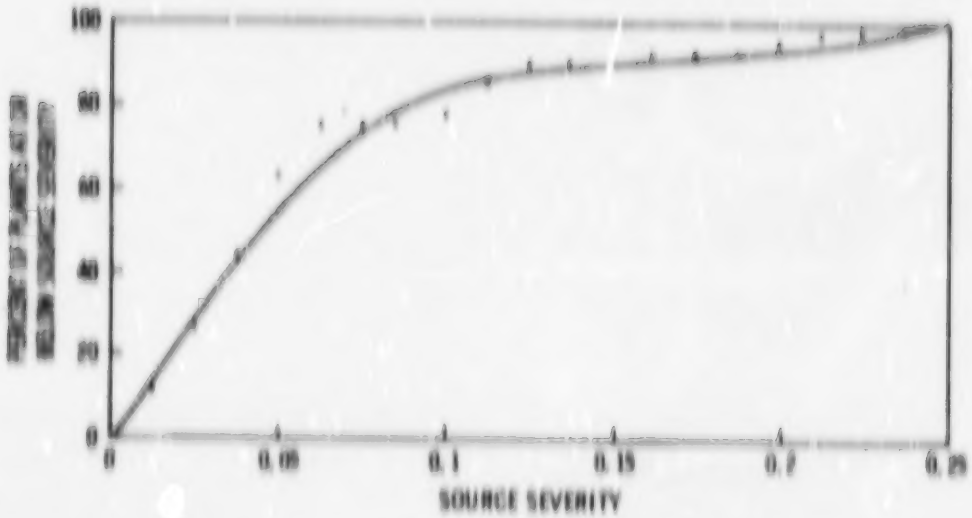

Figure 13. Source severity distribution for high density cooling drums.

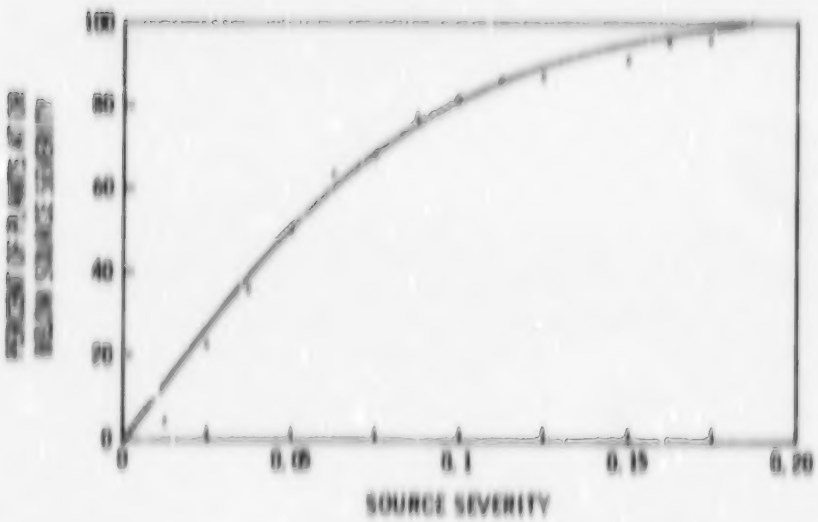

Figure 14. Source severity distribution for the evaporator/ concentrator in low density prilling processes.

capacities for each type of product. (Production capacities were obtained from a confidential Monsanto Company survey.) The percentage of plants having severities in excess of 1.0 and 0.1 for each operation are given in Table 15.

TABLE 15. PERCENT OF PLANTS EXCEEDING SPECIFIED VALUES OF SOURCE SEVERITY, S

	Percent of plants	
	For S = 0.1	For S = 1.0
Solutions and high density prills		
Neutralizer	100	63
Evaporator/concentrator	95	10
Prilling tower	56	0
Cooler	22	0
Low density prills		
Neutralizer	0	0
Evaporator/concentrator	10	0
Prilling tower	5	0
Finishing section	0	0

Another measure of potential environmental effect, the affected population for each pollutant, is also shown in Table 14. The affected population is defined as the number of persons who reside in the area around an average process where the source severity is >1.0. The equations and rationale for the calculation of the affected population are given in Appendix D. For ammonia emissions from the neutralizer, the affected population ranges from 0 to 1,058.

Whereas the source severity and affected population indicate potential effects of emissions from ammonium nitrate manufacturing on a local scale, the national and state emission burdens measure the impact of emissions on a whole area. The particulate emission burden is defined as the ratio of particulates emitted from all ammonium nitrate production statewide or nationwide to the total particulates emitted from all stationary sources in the state or nation. Table 16 is a compilation of particulate emission burdens for each state that produces ammonium nitrate. Calculations were based on state ammonium nitrate capacities as given in Appendix A and the average emission factors in Tables 13 and 14. It was assumed that 39% of the capacity in each state was for a liquid product and 61% for a solid product. Solids were assumed to be 60% high density prills and 40% low density prills. Fugitive emissions (e.g., coating) were not considered in the totals. Total

TABLE 10. PARTICULATE EMISSIONS FROM AMMONIUM NITRATE PLANTS BY STATE

State	Total state particulate emissions, 10^3 metric tons/yr	Total state capacity, 10^3 metric tons/yr	Ammonium nitrate particulate emissions, metric tons/yr	State particulate emission burden
Alabama	1,179	193	340	0.016
Arizona	73	113	205	0.149
Arkansas	130	340	795	0.576
California	1,000	271	617	0.061
Colorado	301	15	38	0.018
Florida	838	388	838	0.170
Georgia	403	456	1,129	0.279
Idaho	55	18	41	0.074
Illinois	1,141	318	728	0.051
Indiana	748	141	321	0.041
Iowa	316	340	795	0.388
Kansas	340	816	1,858	0.514
Kentucky	546	91	207	0.040
Louisiana	381	594	1,358	0.355
Minnesota	366	208	474	0.178
Mississippi	168	454	1,034	0.615
Missouri	302	819	1,865	0.921
Nebraska	95	520	1,184	1.25
New Jersey	153	45	102	0.067
New York	471	64	146	0.031
North Carolina	481	560	1,275	0.265
Ohio	1,766	151	344	0.019
Oklahoma	94	316	720	0.765
Oregon	169	23	52	0.031
Pennsylvania	1,811	150	342	0.019
Tennessee	410	116	264	0.064
Texas	949	440	1,002	0.106
Utah	72	91	207	0.288
Washington	169	161	371	0.229
Wyoming	75	71	166	0.222
All other states	4,264	0	0	-a
U.S. TOTAL	17,871	9,285	19,865	0.106[b]

[a] This category is not applicable for all other states since they have no ammonium nitrate production facilities and therefore no state particulate burden.

[b] National emission burden of ammonium nitrate. Calculated by dividing the total ammonium nitrate emissions by the total particulate emissions for the United States times 100.

state particulate emissions were obtained from the 1972 National Emissions Report (17).

Nebraska's burden (1.2%) exceeds 1.0% of the state totals for particulates; in 16 other states, the particulate emission burdens

(17) 1972 National Emissions Report. EPA-450/2-74-012, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 422 pp.

due to ammonium nitrate manufacturing exceed 0.1%; and the national particulate emission burden for the industry is 0.14%.

SECTION V

CONTROL TECHNOLOGY

A. PARTICULATES

Control technology in the ammonium nitrate industry is primarily concerned with the removal of particulates from the exhausts of the neutraliser, evaporator/concentrator, prilling tower, dryer system, and cooler. These emissions are visible, and state regulations limit both opacity and total particulate emissions.

The particulate emissions from ammonium nitrate production are of two major types, fine (<3 μm) and coarse (≈1 mm). Particulates from the neutraliser, evaporator/concentrator and prilling tower are primarily (>70%) <3 μm in size (12). Table 17 lists the weight percentages of the particles in the neutraliser and high density prilling tower gas exit streams. These fine particles are caused by the dissociation of the NH_4NO_3 solution at high temperatures and recombination of the resulting NH_3 and HNO_3 molecules.

TABLE 17. PARTICLE SIZE DISTRIBUTION IN THE NEUTRALISER AND HIGH DENSITY PRILLING TOWER AIRSTREAMS (12)

Particle size, μm	Weight percent
Neutraliser	
>3	35
1 to 3	25
0.5 to 1	40
0.1 to 0.5	8
<0.1	2
High density prilling tower	
>3	30
1 to 3	20
0.5 to 1	35
<0.5	15

The coarser particles (≈1 mm in diameter) that come from the drying and cooling operations are entrained in the cooling or drying airstream. These emissions are commonly controlled by a high efficiency (99%) wet scrubber. As stated previously, some plants

only have medium efficiency (85%) scrubbers. However, since the particles emitted from these operations are between 10 μm and 1,000 μm, either system will function equally well in meeting state limitations.

Collection of microprills, formed primarily in prilling, is a problem because normal wet scrubbers are not highly (>90%) efficient for particles <3 μm. However, the scrubbers employed in the past did remove particles above 3 μm, which met regulations for weight emissions. A more efficient system was needed since this removal did not place the exit stream within opacity regulations.

The Cooperative Farm Chemicals Association (CFCA) has developed a collection system which minimizes the cost of removing microprills from the prill tower exhaust by reducing the amount of air that must be treated. Since microprills are formed as a result of thermal stresses in the ammonium nitrate droplet shortly after it leaves the spray nozzle, CFCA decided to segregate the air immediately around the nozzle and not to treat all of the air used in the tower. This involved the design and construction of the collection cone shown in Figure 15. While this cone is not a removal system, it greatly reduces the amount of air needing treatment by any proposed removal system.

Monsanto Enviro-Chem Systems, Inc. has developed a Brink® mist eliminator unit which is compatible with the CFCA cone (12). The unit will also accept input from the neutralizer and the evaporator/concentrator as shown in Figure 16. In a typical high density installation the combined streams pass through Brink spray catcher elements, then through Brink high efficiency elements. Each of these elements serves to remove particles by inertial impaction, direct interception and Brownian movement. The spray catcher element removes particles >1 μm with only 250 Pa to 500 Pa pressure drop. As shown in Figure 17, the high efficiency element removes 99% of all particles <3 μm. The efficiency curve for a venturi scrubber (7.47 kPa) is shown for comparison.

Figure 16 depicts a typical high density installation. Its various elements and one not shown, the high velocity elements, can be recombined in several ways to attain the required efficiency for each installation. Standard removal efficiencies for such installations are 90% to 99.5%, and special designs are available for higher removal efficiencies as the need arises. Actual in-line test measurements have shown a Brink unit to be 98.6% efficient on a stream containing neutralizer, evaporator/concentrator and prilling tower (with the CFCA cone) effluents. It should be noted that Brink elements tend to deteriorate in a basic atmosphere. This could pose a problem when using the Brink unit on a combined prill tower/neutralizer stream.

The Brink unit/CFCA cone control technology has also been shown to reduce the opacity of prill tower emission. In one test case

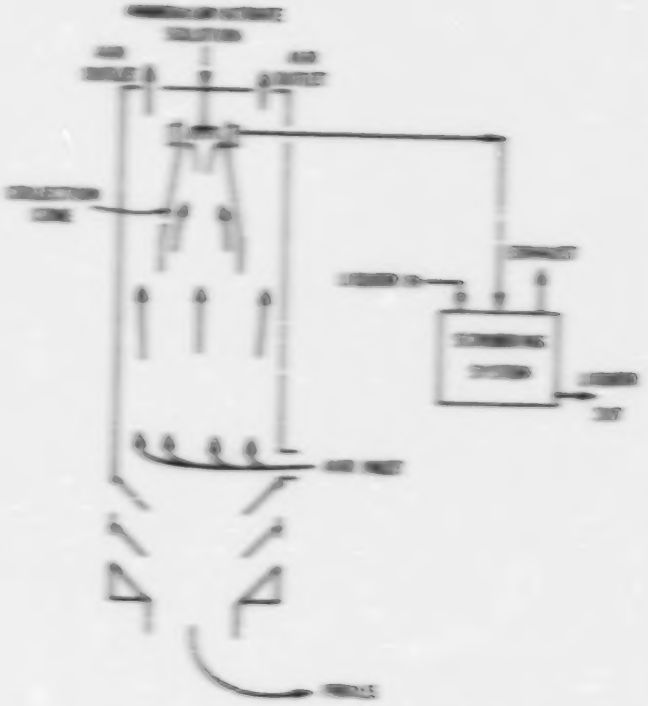

Figure 15. Drilling tower showing placement and operation of the CPCA collecting cone.

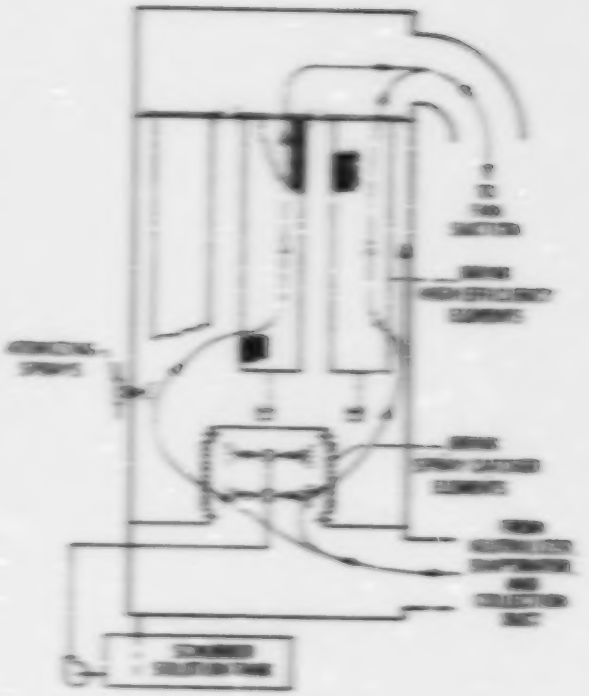

Figure 16. Full-scale brine collection unit.

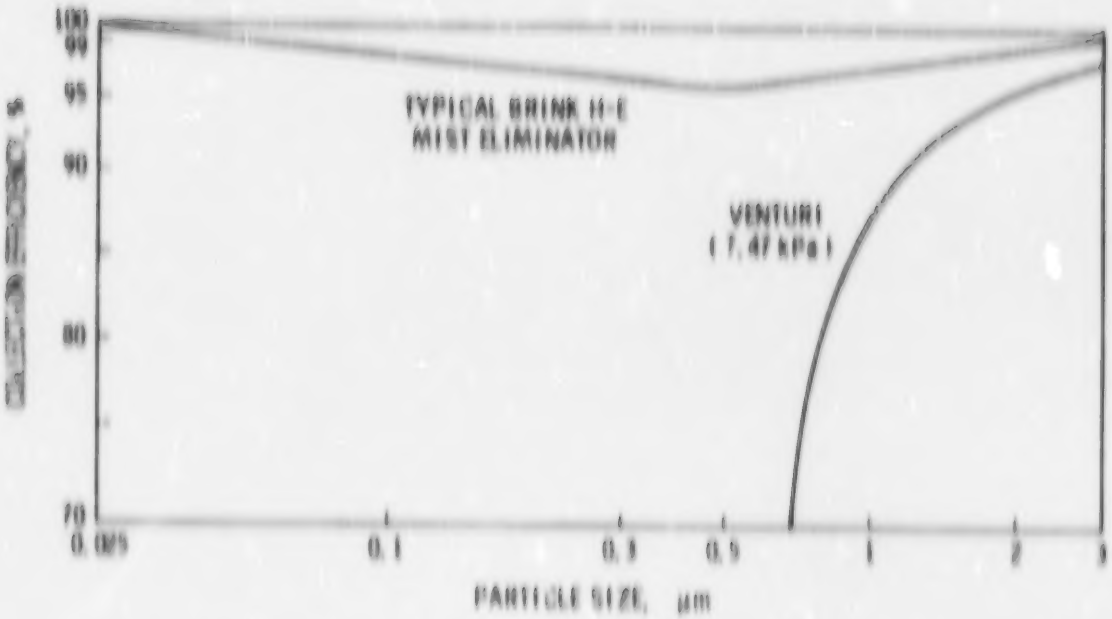

Figure 17. Brink high efficiency element collection efficiency.

(18), where a plant was exceeding the 40% opacity allowed by state code, a Brink unit was installed and opacity levels were reduced to 9.3% and 10.2%, as read by state inspectors.

At least seven plants have Brink units operating or on order, representing 21% of the total industry solution capacity or 57% of the total high density capacity. At least two other plants have controls of some sort on their prill towers (18).

Mississippi Chemical Corporation (MCC) has developed other methods to control neutralizer and prill tower ammonium nitrate emissions (19). MCC engineers have developed and patented a new type of neutralizer that reduces the release of particulates and fumes to only a fraction of those emitted from most neutralizers; a reduction on the order of 10-fold to 20-fold is claimed (19). Emissions of ammonium nitrate, nitric acid and ammonia are brought under control by the use of the patented design and by the close pH control of the neutralizer which is possible only with this new design. MCC offers this design under license agreement to other companies. Emissions from the neutralizer have been found to run <1 kg of ammonia and 0.5 kg of ammonium nitrate per metric ton of ammonium nitrate production.

(18) Personal communication with T. R. Metzger, Monsanto Enviro-Chem Systems, Inc., St. Louis, Missouri, May 1976.

(19) Personal communication with M. L. Brown, Mississippi Chemical Corporation, Yazoo City, Mississippi, May 1976.

A scrubber designed by Beco Engineering Company also controls prill tower emissions (19). These scrubbing units can usually be fitted directly on top of the prill tower a few feet above the sprayheads. Each scrubber consists of module units of packing which may be inserted across the tower. Pilot plant tests have shown efficiencies >90%. NCC has two prill towers in operation with a Beco scrubbing system on each tower (19).

B. AMMONIA OR NITRIC ACID

Emissions of ammonia or nitric acid result from the addition of one of these chemicals in excess to the neutraliser. Control therefore begins with the proper regulation of the pH in the neutraliser. Apparently plants may or may not monitor this parameter closely, so that ammonia emissions could be >1 g/kg of product. There has been no impetus to develop elaborate monitoring systems because the quantity of ammonia usually lost is relatively small (<1 g/kg or less) and no emission regulations are exceeded. The chemical industry as a whole has developed sophisticated monitoring systems that could be applied in this situation, if the need arose.

Where a wet collection device is used to control particulates from the neutraliser, it can also be employed to control ammonia or HNO_3 resulting from normal plant operation. This only requires the maintenance of acidic (or basic) conditions in the scrubbing solution. No information is available on the efficiency of such controls.

C. POTENTIAL IMPACT OF CONTROLS

The potential impact of controls on the emissions from an ammonium nitrate facility is illustrated by the values in Table 18. The emission parameters presented are derived from applying a CFCA cone to the prilling tower and then combining the exhaust stream from the cone with the exhausts from the neutraliser and the evaporator/concentrator. This combined stream is passed through a Brink unit for removal of 98.6% of the particulates. A high-efficiency wet scrubber removes particulate from the cooler. The above mentioned controls are expected to reduce emissions to zero. Since ammonia deteriorates the glass fiber packing used in the Brink unit, the amount of excess NH_3 fed to the neutraliser will be controlled to a low level. This small excess will then be absorbed in the control system.

D. FUTURE CONSIDERATIONS

In the future, the basic problem facing ammonium nitrate manufacturers is compliance with state opacity regulations. This is a particular problem with ammonium nitrate production. Limitations on emissions weight can be met, for example, with wet scrubbers. However, because of the submicron size of the particulate emission, more stringent control technology must be applied to comply with opacity regulations.

TABLE 18. CONTROLLED PARTICULATE EMISSIONS

Emission parameter	Brink unit	Controlled cooler
Emission factor, g/kg	0.049	0.05
Emission rate, g/s	0.191[a]	0.15
$\bar{\chi}_{max}$, µg/m³	51.5[b]	16[c]
Source severity	0.20	0.06
Affected population, persons	0	0

[a]Emission rate determined by 98.6% removal from emission rates of composite stream, not by multiplying the emission factor by total original solution capacity.

[b]Height of Brink is ∿8 m.

[c]Height of scrubber stack is ∿13.7 m.

SECTION VI

GROWTH AND NATURE OF THE INDUSTRY

A. PRESENT TECHNOLOGY

Ammonium nitrate production technology is well developed. There have been no major breakthroughs or developments since high density prilling was begun in the early 1960's. For this reason not many variations exist in the basic process.

In the other processes discussed, there is also little room for change except in equipment design. The plants using such processes differ from prill plants not only in materials flow, but also in product. Some plants have more than one method of forming solids so that their product type can be varied to meet market demand. At least one plant is known to have a prilling tower, graining kettles, and a Sandvik belt.

B. EMERGING TECHNOLOGY

Changes in neutraliser operation are among the most significant emerging developments that may affect emissions. Neutralisation can be carried out under pressure or vacuum as well as at atmospheric conditions. Pressure neutralisation gives maximum economy since the steam produced is used to concentrate the ammonium nitrate solution and to preheat the nitric acid. However, additional control equipment must be used to control excess ammonia in the contaminated condensate.

In 1967, American Cyanamid Company started operation of a vacuum neutraliser at their Hannibal, Missouri, ammonium nitrate plant (20). Operating conditions were adjusted so that stainless steel could be used as the construction material rather than the normal titanium steel. Also, the solution is concentrated to 95%, instead of the normal 83%. If this type of design were implemented throughout the industry, the need for an evaporator in the low density process would be eliminated.

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(20) Falck-Muus, R. New Process Solves Nitrate Corrosion. Chemical Engineering, 74(14):108-116, 1967.

C. INDUSTRY PRODUCTION TRENDS

Figure 18 illustrates actual growth in the ammonium nitrate industry from 1960 to 1975 and the projected growth through 1980 (1). The ammonium nitrate industry continues to be the largest single end-chemical user of nitrogen from ammonia, consuming about 21% of domestic synthetic ammonia production in 1974.

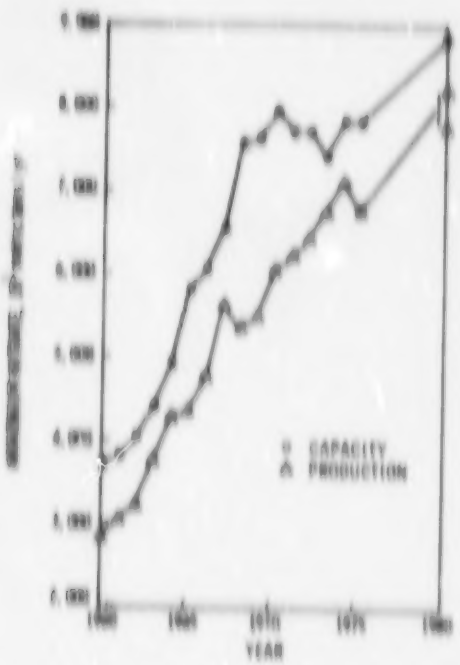

Figure 18. Capacity and production trends.

Table 19 gives ammonium nitrate production data by end use for 1976 (21). Approximately 6.1% of ammonium nitrate produced was as a solution intended for direct sale; 27.7% as a solution for use in the manufacture of nitrogen solutions or other fertilizer materials; 50.3% as a solid; and 15.8% intended for other uses such as the manufacture of explosives.

Ammonium nitrate production is expected to increase at an average rate of 2% per year through 1978. If no additional controls are installed in the industry, particulate emissions in 1978 should be 11% greater than in 1972. However, new controls are being added.

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(21) Current Industrial Reports, Inorganic Fertilizer Materials and Related Products. Series M28A(76)-1 through M28A(76)-12, U.S. Department of Commerce, Washington, D.C., January through December 1976. 6 pp. each.

TABLE 19. PRODUCTION OF AMMONIUM NITRATE BY END USE, 1978

Production	Metric tons/yr
Fertilizer	
Liquid for direct sale	476,781
Liquid for consumption in other nitrogen fertilizers	2,107,567
Solid	3,831,839
Subtotal	6,329,089
Other uses	1,159,074
Production total	7,588,173

and the relative amount of ammonium nitrate solutions as a final product versus solids is increasing. Therefore, 1978 emissions may be lower than those in 1972 even with increased production.

REFERENCES

1. Personal communication with E. A. Harre, National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, Alabama, June 1976.

2. Williams, L., L. F. Wright, and R. Hendrika. Process for the Production of Ammonium Nitrate. U.S. Patent 2,402,192 (to Consolidated Mining and Smelting Co. of Canada, Ltd.), June 18, 1946.

3. Shearon, W. H., Jr., and W. S. Dunwoody. Ammonium Nitrate. Industrial and Engineering Chemistry, 45(3):496-504, 1953.

4. Sharp, J. C. Nitrogen. In: Chemistry and Technology of Fertilisers, V. Sauchelli, ed. Reinhold Publishing Corporation, New York, New York, 1960. pp. 26-32.

5. Miller, P., and W. C. Seaman. Properties of Monocrystalline Ammonium Nitrate Fertilizer. Industrial and Engineering Chemistry, 40(1):154-160, 1948.

6. Slack, A. V. Fertiliser Developments and Trends - 1968. Noyes Development Corporation, Park Ridge, New Jersey, 1968. 405 pp.

7. Ammonium Nitrate. In: Riegel's Handbook of Industrial Chemistry, J. A. Kent, ed. Van Nostrand Reinhold Company, New York, New York, 1974. pp. 100-101.

8. Hester, A. S., J. J. Dorsey, Jr., and J. T. Kaufman. Stengel Process Ammonium Nitrate. Industrial and Engineering Chemistry, 46(4):622-632, 1954.

9. Stengel, I. A. Process for Producing Ammonium Nitrate. U.S. Patent 2,568,901 (to Commercial Solvents Corp.), September 25, 1951.

10. Dorsey, J. J. Ammonium Nitrate by the Stengel Process. Industrial and Engineering Chemistry, 47(1):11-17, 1955.

11. Volk, W. Applied Statistics for Engineers, Second Edition. McGraw-Hill Book Co., New York, New York, 1969. 354 pp.

12. Metzger, T. R. Controlling Airborne Emissions from Ammonium Nitrate Production. Presented to Ammonium Nitrate Study Group, Sarnia, Ontario, August 1974. 7 pp.

13. Feick, G., and R. M. Hainer. On the Thermal Decomposition of Ammonium Nitrate. Steady-State Reaction Temperatures and Reaction Rate. Journal of the American Chemical Society, 76(23):5860-5863, 1954.

14. Ammonia. In: The Merck Index, P. G. Stecher, ed. Merck and Company, Inc., Rahway, New Jersey, 1960. p. 64.

15. Matheson Gas Data Book. The Matheson Company, Inc., East Rutherford, New Jersey, 1966. pp. 13-22.

16. Point Source Listings. National Emissions Data System. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1974.

17. 1972 National Emissions Report. EPA-450/2-74-012, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 422 pp.

18. Personal communication with T. R. Metzger, Monsanto Enviro-Chem Systems, Inc., St. Louis, Missouri, May 1976.

19. Personal communication with M. L. Brown, Mississippi Chemical Corporation, Yazoo City, Mississippi, May 1976.

20. Falck-Muus, R. New Process Solves Nitrate Corrosion. Chemical Engineering, 74(14):108-116, 1967.

21. Current Industrial Reports, Inorganic Fertilizer Materials and Related Products. Series M28B(76)-1 through M28B(76)-12, U.S. Department of Commerce, Washington, D.C., January through December 1976. 6 pp. each.

22. TLVs® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1975. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1975. 97 pp.

23. Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, May 1970. 84 pp.

24. Hesketh, H. E. Understanding and Controlling Air Pollution. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 1974. p. 63.

35. Bimutis, E. C., and M. G. Konicek. Derivations of Continuous Functions for the Lateral and Vertical Atmospheric Dispersion Coefficients. Atmospheric Environment, 6(11):859-863, 1972.

36. Metric Practice Guide. ASTM Designation: E 380-74, American Society for Testing and Materials, Philadelphia, Pennsylvania, November 1974. 34 pp.

APPENDIX A

RAW DATA USED TO CALCULATE EMISSION FACTORS AND PLANT CHARACTERISTICS

Table A-1 (1) is a list of 64 ammonium nitrate plants giving location, population density of the county or parish in which each is located, and annual capacity.

Table A-2 is a compilation of data obtained from the National Emissions Data System, from private industry, and from field observations. All emission factors indicated are from source measurements.

Table A-3 is a compilation of particulate emission factors from prilling operations.

Table A-4 is a listing of stack heights for various points in an ammonium nitrate manufacturing plant. These values were obtained from private industry contacts and field observations.

TABLE 6-1. AMMONIUM NITRATE PLANT LOCATIONS AND CAPACITIES (1)

Company	City/State	Basis	County or parish population density, persons/sq mi	Annual capacity, 10³ metric tons/yr
Agway, Inc.:	Dixon, NY	Cattaraugus	33.4	54
Air Products and Chemicals, Inc.:	Pensacola, FL	Escambia	116.6	182
Ashland Chemical Corp. Ashland Chemical Division Agricultural Department	[illegible], LA	Ouachita	48.1	191
Agricultural Division	Mansfield, MO	Marion	49.4	181
Apache Powder Co.:	Benson, AZ	Cochise	5.8	113
CF Industries, Inc.: Donaldsonville Nitrogen Complex Plant No. 1 Plant No. 2 Port Neal Nitrogen Complex Woodward Nitrogen Complex	Donaldsonville, LA Port Neal, IA Woodward, OK	Ascension Woodbury Dewey	110.2 87.8 [illegible]	410 [illegible] [illegible]
Chemical Energy Corp. Division of Interstate Brands Corp. (bankrupt) Mylan Chemical Co. (abandoned)	Chaparral, NM	Lincoln	20.5	11
Columbia Nitrogen Corp.:	Augusta, GA	Richmond	691.0	113
Conison American, Inc.:	Hastings, NE	Hays	33.5	154
Cooperative Farm Chemicals Association	Lawrence, KS	Douglas	100.1	617
E. I. duPont de Nemours & Co., Inc. Agricultural Chemicals Department Petroleum Laboratories Department	Gibbstown, NJ Old Hickory, TN Memphis, TN Beaumont, TX	Gloucester Shelby Shelby Jefferson	340.8 [illegible] [illegible] [illegible]	91 [illegible] [illegible] [illegible]
Farmland Industries, Inc.:	Dodge City, KS	Ford	7.8	11
Gardinier Big River, Inc.:	Mulberry, FL	Polk	57.8	91
Gardinetown, Inc.:	Augusta, GA	Richmond	11.7	10
W. R. Grace & Co. Agricultural Chemicals Group	Birmingham, AL	Jefferson	33.1	191
Hyde Oil Corp. Hyde Oil Companies Co. Industrial and Specialty Chemicals Division	Pittsburg, KS	Crawford	32.9	135
Hercules, Inc. Industrial Systems Department	Hopewell, VA Louisiana, MO	Hopewell Pike	[illegible] [illegible]	[illegible] [illegible]
Synthetics Department	Parlin, NJ Brunswick, GA	Middlesex Glynn	1,000.0 [illegible]	[illegible] [illegible]
Illinois Nitrogen Co.:	Hopkinsville, IL	Caldwell	93.9	136
International Minerals & Chemicals Corp.:	Sterlington, LA	Union	19.1	170
Kaiser Aluminum & Chemicals Corp. Kaiser Agricultural Chemicals Division	Baton Rouge, LA Chalmette, LA Tampa, FL	Ascension Pointe Coupee Hillsborough	[illegible] [illegible] [illegible]	[illegible] [illegible] [illegible]
Lone Star Gas Co.: Bloom, Inc. (subsidiary)	Borger, TX	Hutchinson	17.9	91
Mississippi Chemical Corp.:	Yazoo City, MS	Yazoo	28.9	454
Mobil Oil Corp. Mobil Chemical Co. Petrochemicals Division	Beaumont, TX	Jefferson	251.1	111
Monsanto Co.: Missouri Agricultural Products Co.	St. Rose, LA Luling, LA	Union St. Charles	91.5 91.5	123 123
Nitram, Inc.:	Tampa, FL	Hillsborough	466.9	136
O-Bee Corp.: Chickasaw Nitrogen Division	Pryor, OK	Mayes	33.1	11
Occidental Petroleum Corp.: Hooker Chemical Co. (subsidiary)	Hanford, CA	Kings	14.9	11

*This plant obtains solutions from another facility and produces captive grained product.

(continued)

Table A-1 (continued)

Company	City/State	County or parish	Population density, persons/km²	Annual production, 10³ metric tons/yr
Phillips Pacific Chemical Co.	Commerce, NV	Boston	10.5	50
[illegible]	[illegible], NV	[illegible]	22.5	450
Reichhold Chemicals, Inc.	St. Helens, OR	Columbia	44.5	21
U. Paul Ammonia Products, Inc.	St. Paul, MN	Dakota	160.7	330
[illegible] Nitrate Chemicals Division	Pocatello, ID	Bannock	65.5	10
[illegible] Chemical Co. (subsidiary)	Clinton, IA	Clinton	51.5	135
[illegible]	[illegible], IA	Linn	10.5	22
The Standard Oil Co. (Ohio) [illegible]	Lima, OH	Allen	170.5	50
Tennessee Valley Authority	Muscle Shoals, AL	Colbert	52.1	10
Terra Chemicals International, Inc.	[illegible]	Woodbury	44.5	130
[illegible]	[illegible]	[illegible]	107.5	150
Union Oil Co. of California [illegible]	Brea, CA	Orange	1,002.5	55
[illegible]	[illegible], MO	[illegible]	150.5	55
Valley Nitrogen Producers, Inc.	[illegible], CA	[illegible]	52.1	80
The Williams Companies (subsidiary)	[illegible], AZ	Henderson	61.5	450
TOTAL				3,101

TABLE A-2. AMMONIUM NITRATE PLANT PARTICULATE EMISSION FACTORS (g/kg)

Plant	Neutral-izer	Dryer/ cooler	Prill tower	Dryer	Cooler
A	0.22	0.04	0.11	0.33	
B	0.14	0.02	1.09		
C			0.78		
D			0.65	0.71	
E	0.59				5.13[a]
F			1.03		
G			1.22		
H			1.80	0.65	
I	0.15				
J	1.0				
K	1.5				
L	0.1				
M	1.1				
Mean	1.01	0.01	1.00	0.34	5.13
Standard deviation	1.01	0.01	1.11	0.37	

[a]No control device; assume for representative plant that a 99% efficient scrubber would be added.

Note: Blanks in table indicate data not available.

TABLE A-3. PRILL TOWER EMISSIONS[a]
(g/kg)

0.61	1.46	1.19	1.30	1.28	0.87	1.16	1.11	1.64
1.70	2.44	3.36	1.64	1.47	1.28	1.05	2.17	1.05
1.51	0.66	0.74	1.16	1.46	1.25	1.11	0.85	1.12
1.26	1.23	1.30	1.36	1.07	1.24	1.28	2.09	1.31
1.38	1.43	0.77	1.55	1.26	1.78	0.95	0.94	1.21
1.54	1.80	1.45	1.36	1.10	1.35	1.14	0.97	1.92
1.12	1.21	1.29	0.87	0.80	1.19	1.32	0.78	1.24
0.88	1.56	1.01	1.31					

[a]Data received from a private industry source.

TABLE A-4. REPRESENTATIVE STACK HEIGHTS (16)
(meters)

Plant	Neutraliser	Evaporator	Prilling tower	Dryer	Cooler
A	9.75	13.11	46.63	7.92	7.92
B	20.73	18.9	56.96		
C		12.98	56.19		
D			17.49	15.32	
E			21.3		
F			17.15	14.61	14.61
G			10.46		
H		9.81	15.01	10.98	10.98
I			50.29		
J			13.53		
K			46.94		
L			42.67		
M			48.45		
N			18.10		
O			28.04		
P			14.62		
Q			16.58		
R			60.96		
Average	15.2	13.7	41.2	13.7	13.2

Note: Blanks in table indicate data not available.

APPENDIX A

DERIVATION OF SOURCE SEVERITY EQUATIONS

The potential effect of the emissions from ammonium nitrate production on ambient air quality can be evaluated by comparing the time averaged maximum ground level concentration, χ_{max}, to the ambient air quality standard or a reduced threshold limit value, TLV (22) for noncriteria pollutants for each emission.

An initial calculation of the instantaneous (3 minutes) maximum ground level concentration, χ_{max}, must first be made. For an elevated point source in neutral atmospheric conditions (atmospheric stability class C), the following equation is applicable (23):

$$\chi_{max} = \frac{2\,Q}{\pi e u h^2} \qquad \text{(B-1)}$$

where Q = pollutant emission rate, g/s
u = average wind speed, m/s
h = effective stack height, m
e = 2.72
π = 3.14

Equation B-1 is the solution to the Turner plume dispersion equation (23) at that distance downwind from the source for which the ground level concentration is a maximum. The χ_{max} equation does not establish the point where χ_{max} occurs with respect to the source, but it does determine the maximum instantaneous ground level concentration of the emission species.

(22) TLVs® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1975. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1975. 97 pp.

(23) Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, May 1970. 84 pp.

The severity of an emission source can be calculated by the general equation:

$$S = \frac{\bar{x}_{max}}{F} \qquad (B\text{-}2)$$

where S = source severity
$\bar{x}_{max}$ = average maximum ground level concentration over a defined averaging period, g/m³
F = hazard factor, g/m³

The quantity F in Equation B-2 is equal to the ambient air quality standard for criteria pollutants (i.e., CO, SO_x, NO_x, hydrocarbons, and particulates). For noncriteria pollutants, F is calculated by the following equation:

$$F = TLV \cdot \frac{8}{24} \cdot \frac{1}{100} \qquad (B\text{-}1)$$

where TLV = threshold limit value of the emitted material, g/m³
8/24 = correction factor for the 8-hr work day which is the basis for the TLV
1/100 = safety factor

Values of F for particulates and NO_x are 260 μg/m³ and 100 μg/m³, respectively. The value of F for ammonia, calculated from a TLV of 18 mg/m³, is 60 μg/m³.

The value of $\bar{x}_{max}$ is determined from the value of x_{max} using the following equation:

$$\bar{x}_{max} = x_{max}\left(\frac{t_0}{t}\right)^{0.17} \qquad (B\text{-}4)$$

where t_0 = time of instantaneous maximum ground level concentration determination, i.e., 3 min
t = averaging time for emission species, min
0.17 = curve fitting exponent from correlation

For particulates the averaging time is 24 hr (1,440 min). Using this value in Equation B-4, and substituting Equation B-1 into Equation B-4 and reducing, the following equation results for x_{max} for particulates:

$$\bar{x}_{max} = \frac{0.0182\ Q}{h^2} \qquad (B\text{-}5)$$

The source severity equation for particulates can be derived similarly from Equations B-2 and B-5 to be:

$$S = \frac{70\ Q}{h^2} \qquad (B\text{-}6)$$

The averaging time for ammonia is also 24 hr and F = 60 $\mu g/m^3$; hence:

$$\chi_{max} = \frac{0.0182\ Q}{h^2} \qquad \text{(B-6)}$$

and

$$S = \frac{103\ Q}{h^2} \qquad \text{(B-7)}$$

For nitric acid emissions the averaging time is also 24 hr. If HNO_3 emissions were present the χ_{max} equation would be the same as Equation B-6. From this the following source severity equation is derived, based on the TLV for nitric acid of 5 mg/m^3:

$$S = \frac{1.090\ Q}{h^2} \qquad \text{(B-8)}$$

For situations in which fugitive emissions are released from the confinement of a building, a different type of equation is needed to determine the maximum ground level concentration and related source severity. An equation of this type is (24):

$$\chi_{(x,0,0)} = \frac{Q}{(\pi\ \sigma_y\ \sigma_z + A')\bar{u}} \qquad \text{(B-9)}$$

where $\chi_{(x,0,0)}$ = concentration downwind with no vertical or horizontal component, g/m^3

Q = emission rate, g/s

σ_y, σ_z = horizontal and vertical deviation, m

A' = 1/2 the cross sectional area of the building perpendicular to the flow of the wind, m^2

$\bar{u}$ = mean wind speed = 4.5 m/s

This concentration at the distance to plant boundary (D) is equivalent to χ_{max}. For stability class C, it has been shown that (25):

$$\sigma_y = 0.209\ D^{0.903} \qquad \text{(B-10)}$$

$$\sigma_z = 0.113\ D^{0.911} \qquad \text{(B-11)}$$

where D = distance to plant boundary downwind from source in the horizontal plane, m

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(24) Hesketh, H. E. Understanding and Controlling Air Pollution. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 1974. p. 61.

(25) Bimutis, E. C., and M. G. Konicek. Derivations of Continuous Functions for the Lateral and Vertical Atmospheric Dispersion Coefficients. Atmospheric Environment, 6(11):859-863, 1972.

By substituting B-10 and B-11 into B-9 the following equation is derived:

$$\chi_{max} = \frac{Q}{[(7.42 \times 10^{-5})\, D^{1.914} + A']\, 4.5} \qquad \text{(B-12)}$$

Employing the conversion of χ_{max} given by Equation B-4 for a 24-hr averaging period, the following is derived:

$$\bar{\chi}_{max} = \frac{7.78 \times 10^{-2}\, Q}{(7.42 \times 10^{-5})\, D^{1.914} + A'} \qquad \text{(B-13)}$$

The source severity is then calculated using the particulate ambient air quality standard of 260 $\mu g/m^3$ (24-hr averaging time):

$$S = \frac{299\, Q}{(7.42 \times 10^{-5})\, D^{1.914} + A'} \qquad \text{(B-14)}$$

Equation B-14 is then used to calculate the source severity of emissions from confinement at any given distance, usually the plant boundary.

For a worst case analysis, Equation B-14 can be maximized by allowing A' to approach 0. As a result of this operation, Equation B-15 is derived:

$$S = 4,030\, Q\, D^{-1.914} \qquad \text{(B-15)}$$

and likewise the equation for $\bar{\chi}_{max}$ becomes:

$$\bar{\chi}_{max} = 1.05\, Q\, D^{-1.914} \qquad \text{(B-16)}$$

APPENDIX C

ESTIMATE OF STEAM FROM NEUTRALISER

The quantity of steam liberated from the neutraliser by the heat of reaction is equal to the difference in concentrations of the initial solution and the exiting solution. For an average plant (1.315×10^5 metric tons/yr), concentrating the initial solution from 61% NH_4NO_3 to an exiting solution of 83% releases ~1.45 m^3/s of steam at 150°C and 101 kPa. Another author has indicated that the steam output from a 9.09×10^4 metric ton/yr plant is ~1.12 m^3/s (12). Based on a linear scaleup to average capacity, the quantity becomes 1.62 m^3/s. The lower value is presumably the result of lower steam temperatures and partial condensation.

APPENDIX D

CALCULATION OF AFFECTED POPULATION

Since the χ_{max} equation (Equation B-1) does not contain a downwind distance term, another form of the Gaussian plume equation is needed to find the population affected by plant emissions. The following is a rationale for the calculations.

If the wind directions are taken to 16 points and it is assumed that the wind directions within each sector are distributed randomly over a period of a month or a season, it can further be assumed that the effluent is uniformly distributed in the horizontal within the sector. The appropriate equation for average concentration is then (22):

$$\bar{\chi} = \frac{2}{\pi}\frac{\theta_1}{\sigma_z}\frac{Q}{\theta x}\exp\left[-\frac{1}{2}\left(\frac{h}{\sigma_z}\right)^2\right] \quad (g/m^3) \qquad (D\text{-}1)$$

Since the distances at which severity $\bar{\chi}/F$ equals 1.0 are desired, the roots (R) of the following equation are determined:

$$0 = \left\{\frac{2}{\pi}\frac{\theta_1}{\sigma_z}\frac{Q}{\theta x}\exp\left[-\frac{1}{2}\left(\frac{h}{\sigma_z}\right)^2\right]\right\} - 1.0 \qquad (D\text{-}2)$$

In addition,

$$\sigma_z = ax^b + c \qquad (D\text{-}3)$$

where a, b, and c are functions of atmospheric stability. In this case the atmospheric stability is assumed to be class C and the values of a, b, and c are 0.113, 0.911, and 0.0, respectively.

For a specified emission from a typical source, severity as a function of distance can be represented as follows:

with X_1 and X_2 being the distances from the source where S = 1.0. Sweeping those distances through 6.282 rad an annulus is obtained:

The affected population is then in an area, A:

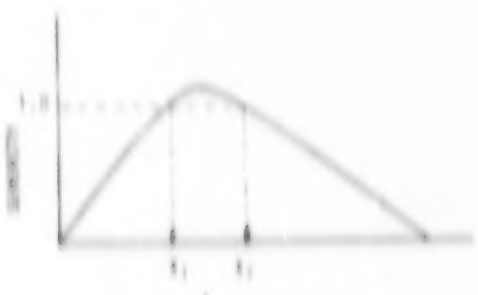
$$A = \pi(X_2^2 - X_1^2) \ (km^2) \qquad (D\text{-}4)$$

If the affected population density is D_p, then the total affected population, P, is:

$$P = D_p A \ (persons) \qquad (D\text{-}5)$$

There could be cases where the downrange severity function appears as follows:

Thus the affected population is zero. In other cases the affected population will be extremely low regardless of population density because the severity for a particular emission may correspond to that shown below and thus result in a small annulus:



GLOSSARY

additive: Any material added to the concentrated ammonium nitrate before solids formation which changes the natural mechanical characteristics of the ammonium nitrate solid particle.

affected population: Number of persons living in the area near a representative plant where the source severity is greater than 1.0.

emission factor: Mass of an emission per unit weight of final product.

emission growth factor: Ratio of emissions for 1978 versus 1972.

emission rate: Mass of emissions per unit time.

fugitive emissions: Gaseous and particulate emissions that result from industrial related operations, but which are not emitted through a primary exhaust system, such as a stack, flue, or control system.

graining: Process in which concentrated ammonium nitrate solution is solidified by placing a concentrated solution in a steam jacket-heated kettle and mixing until the water evaporates.

granulation: Process in which concentrated ammonium nitrate solution is solidified by spraying the concentrated solution on a falling curtain or rolling bed of seed particles to build a larger particle.

high density prills: Prills formed using a 99.5+% solution that lowers the number of void spaces formed to create a more dense prill.

low density prill: Prills formed using a 95% to 96% solution that allows more voids in the final product, giving a less dense prill.

national emission burden: Mass of particulates emitted from the ammonium nitrate industry divided by the total national particulate emissions expressed in percent.

original solution capacity: Capacity of the facility expressed as weight of solution (not final solid product) produced per unit time.

prill: A spherical particle formed by the solidification of an ammonium nitrate droplet.

prilling: Process in which concentrated ammonium nitrate solution is solidified by spraying the concentrated solution in a tower so that the drops formed fall countercurrent to a stream of cooling air.

source severity: Ratio of the ground level concentration of each emission species to its corresponding ambient air quality standard (for criteria pollutants) or to a reduced TLV (for noncriteria emission species).

state emission burden: Mass of particulates emitted from the ammonium nitrate industry in a particular state divided by the total state particulate emissions expressed in percent.

threshold limit value (TLV): Refers to the airborne concentration of a substance and represents conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect for a 7- or 8-hour work-day and 40-hour workweek.

CONVERSION FACTORS AND METRIC PREFIXES (26)

CONVERSION FACTORS

To convert from	to	Multiply by
degree Celsius (°C)	degree Fahrenheit	$t_F^\circ = 1.8\ t_C^\circ + 32$
joule (J)	British thermal unit	9.479×10^{-4}
kilogram (kg)	pound-mass (lb mass avoirdupois)	2.205
kilogram (kg)	ton (short, 2,000 lb mass)	1.102×10^{-3}
kilometer^2 (km^2)	mile^2	3.861×10^{-1}
meter (m)	foot	3.281
meter (m)	mile	6.215×10^{-4}
meter^2 (m^2)	foot^2	1.076×10^{1}
meter^3 (m^3)	foot^3	3.531×10^{1}
metric ton	pound	2.205×10^{3}
pascal (Pa)	atmosphere	9.869×10^{-6}
radian (rad)	degree (°)	5.730×10^{1}

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
k	kilo	10^3	1 kPa = 1×10^3 pascals
m	milli	10^{-3}	1 mm = 1×10^{-3} meter
u	micro	10^{-6}	1 ug = 1×10^{-6} gram

(26) Metric Practice Guide. ASTM Designation E-380-74, American Society for Testing and Materials, Philadelphia, Pennsylvania, November 1974. 34 pp.